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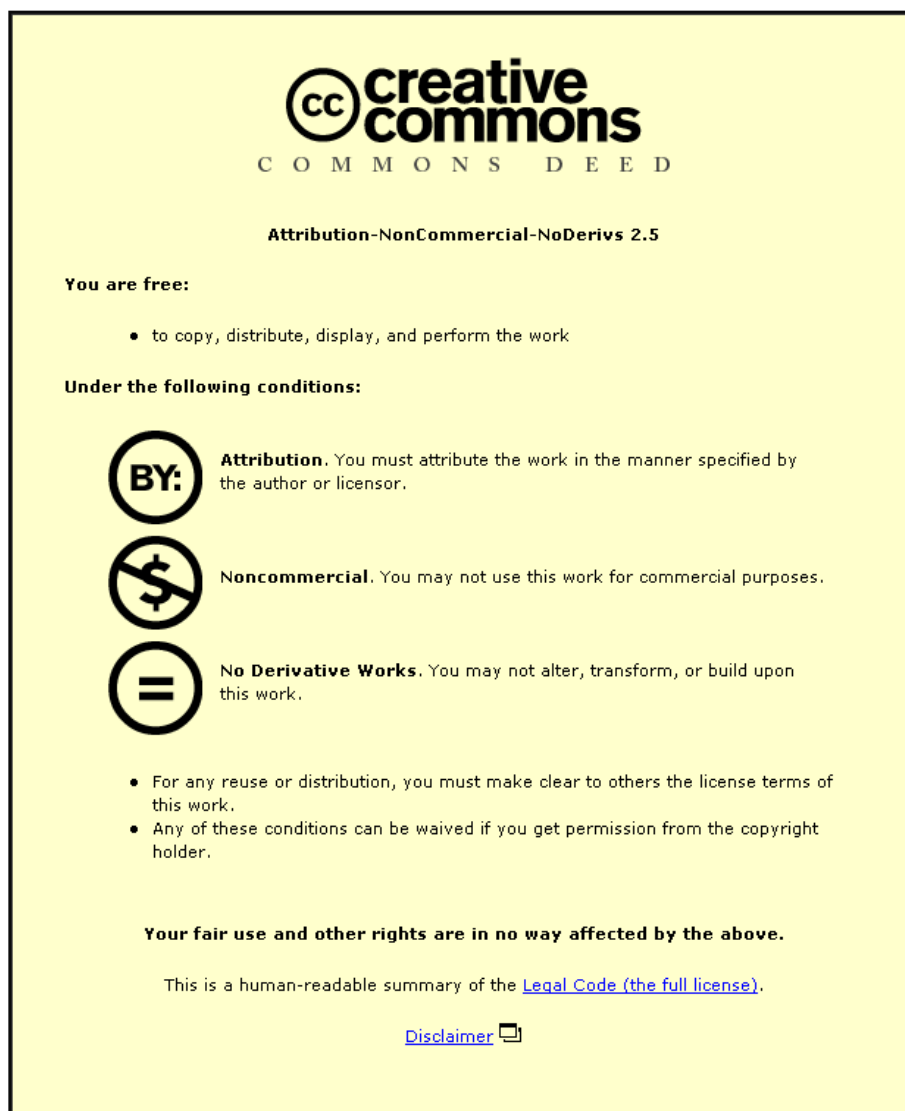
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**New Reactions of Metal-Alkyne Complexes**

by

**Ryan James Davoile**

A Doctoral Thesis


Submitted in partial fulfilment of the requirements

For the award of

Doctor of Philosophy of Loughborough University

(October 2003)

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## Abstract

This thesis describes the use of bimetallic alkyne complexes for use in variants of the Nicholas reaction. The heterobimetallic core provides a source of chiral control unlike previous protocols reported in the literature, as stereocontrol arises from the inherently chiral cobalt-molybdenum core of these complexes and not from an external source.

The inherently chiral heterobimetallic complexes were utilised as efficient chiral auxiliaries for nucleophilic additions to both propargylic alkene and Nicholas salt complexes with a degree of stereocontrol also extending to intramolecular addition.

1,3-Dipolar cycloaddition to homobimetallic and heterobimetallic enyne complexes to obtain isoxazoline ring systems was investigated, following a report in the literature.

A novel homobimetallic 1,3-dipole was synthesised on opening of a cyclopropane, subsequently trapping with a series of aldehyde and imines to efficiently form tetrahydrofuran and pyrrolidine ring structures.

Chapter 1: An overview of developments of homobimetallic alkyne complexes in the Nicholas reaction as reported in the literature.

Chapter 2: Highlights our research into the use of bimetallic alkyne complexes for use in organic synthesis.

Chapter 3: Provides experimental data for our studies.

## Acknowledgements

Firstly I would like to thank Dr. Steve Christie for developing my interest in synthetic organic chemistry and along with Prof. Ray Jones for giving me the opportunity to study towards a Ph.D. The continual support, direction and enthusiasm by them for my project and progress have been invaluable over the last three years. Many thanks go out to the other members of the group, Andy, Emma, Fletch, Jaime, Nige, Ross and Terry for their relentless help, support, friendship and of course the banter.

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## Contents

<b>1.0</b>	<b>Introduction</b>	<b>1</b>
1.1	Binary metal carbonyl complexes	1
1.2	The Nicholas Reaction	3
1.2.1	Reaction Discovery	3
1.2.2	Evidence for [(propargylium)Co <sub>2</sub> (CO) <sub>6</sub> ] <sup>+</sup> cations	3
1.2.3	Generation of [(propargylium)Co <sub>2</sub> (CO) <sub>6</sub> ] <sup>+</sup> cations	5
1.2.4	Nucleophilicity of [(propargylium)Co <sub>2</sub> (CO) <sub>6</sub> ] <sup>+</sup> cations	5
1.3	Reaction with carbon nucleophiles	7
1.3.1	Alkene Nucleophiles	7
1.3.2	Enolate Nucleophiles	11
1.3.3	Allyl Nucleophiles	23
1.3.4	Aromatic Nucleophiles	28
1.4	Reaction with oxygen nucleophiles	32
1.5	Reaction with other heteroatom nucleophiles	44
1.5.1	Azide Nucleophiles	44
1.5.2	Amine Nucleophiles	44
1.5.3	Sulfur Nucleophiles	46
1.5.4	Fluoride Nucleophiles	47
1.6	Extension of Nicholas methodology	49
<b>2.0</b>	<b>Results and Discussion</b>	<b>52</b>
2.1	Heterobimetallic alkyne systems	52
2.1.1	Background	52
2.1.2	Enantiospecific rationale for the heterobimetallic core	52
2.1.3	Synthesis of the heterobimetallic core	53
2.2	Exploration of heterobimetallic Nicholas salt complexes	57
2.2.1	Grignard addition to heterobimetallic-butynal	57
2.2.2	Synthesis of heterobimetallic Nicholas salts	60
2.2.3	Nucleophilic addition to Nicholas salt complexes	62

2.2.4	Using Nicholas methodology in the formation of enynes	65
2.2.5	Nucleophilic addition to protonated alkene complexes	66
2.3	Intramolecular nucleophilic addition to form ring systems	70
2.3.1	Grignard addition to heterobimetallic aldehyde	71
2.3.2	Cyclisation using Nicholas methodology	73
2.3.3	Application to a carbenoid precursor	75
2.4	1,3-Dipolar cycloadditions with bimetallic systems	77
2.4.1	Background	77
2.4.2	Homobimetallic 1,3-dipolar cycloadditions	79
2.4.3	Heterobimetallic 1,3-dipolar cycloadditions	82
2.4.4	Desymmetrised 1,3-dipolar cycloadditions	88
2.4.5	Synthesis of furan derivatives using carbonyl ylids	91
2.5	Novel trapping of Nicholas stabilised ring opened cyclopropanes	94
2.5.1	Background	94
2.5.2	Development of the homobimetallic cyclopropane	94
2.5.3	Optimisation studies	96
2.5.4	Cyclisation with aldehydes	99
2.5.5	Cyclisation with imines	104
2.6	Conclusion	109
2.7	Future Plans	113
3.0	<b>Experimental</b>	116
4.0	<b>References</b>	207
5.0	<b>Appendices</b>	
	X-Ray crystallographic data for Dicobalt hexacarbonyl-5-ethynyl-2-(4-nitrophenyl)tetrahydrofuran-3,3-dicarboxylic acid dimethyl ester	

## Abbreviations

Ac	=	acetyl
aq	=	aqueous
approx	=	approximately
Ar	=	aryl
Bn	=	benzyl
Bu	=	butyl
<i>i</i> -Bu (or <sup>i</sup> Bu)	=	<i>iso</i> -butyl
<i>n</i> -Bu (or <sup>n</sup> Bu)	=	normal butyl
<i>t</i> -Bu (or <sup>t</sup> Bu)	=	tertiary butyl
CAN	=	ceric ammonium nitrate
cat	=	catalyst
cm <sup>3</sup>	=	cubic centimetre
cm <sup>-1</sup>	=	wave number
°C	=	degrees Celcius
Cp	=	cyclopentadienyl
Cy	=	cyclohexyl
δ	=	chemical shift
d	=	doublet
DABCO	=	1,4-diazabicyclo[2.2.2]octane
DAST	=	diethylaminosulfur trifluoride
DBU	=	1,8-diazabicyclo[5.4.0]undec-7-ene
DCM	=	dichloromethane
dd	=	doublet of doublets
DDQ	=	2,3-dichloro-5,6-dicyano-1,4-benzoquinone
d.e.	=	diastereoisomeric excess
DME	=	dimethoxyethane
DMS	=	dimethylsulfide
d.r.	=	diastereoisomeric ratio
e.e.	=	enantiomeric excess
EI	=	electron ionisation
eq (or equiv.)	=	equivalent

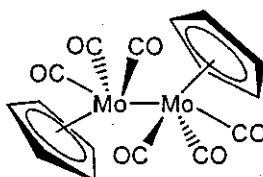
Et	=	ethyl
EtOH	=	ethanol
EWG	=	electron withdrawing group
FAB	=	fast atom bombardment
g	=	gram
h	=	hour(s)
<i>n</i> -hexane	=	normal hexane
Hz	=	Hertz
IR	=	infra-red
LDA	=	lithium diisopropylamine
m	=	multiplet
<i>m</i> -CPBA	=	<i>meta</i> -chlorobenzoic acid
MeOH	=	methanol
Me	=	methyl
MeCN	=	acetonitrile
MHz	=	Megahertz
min	=	minutes
mL	=	millilitre
mmol	=	millimole(s)
mM	=	millimolar
Mol Sieves	=	4Å molecular sieves
mp	=	melting point
Ms	=	mesyl
<i>m/z</i>	=	mass to charge ratio
MS	=	Mass Spectroscopy
MW	=	molecular weight
n/a	=	not applicable
NBS	=	<i>N</i> -bromosuccinimide
NCS	=	<i>N</i> -chlorosuccinimide
NMR	=	Nuclear Magnetic Resonance
NMO	=	<i>N</i> -methylmorpholine- <i>N</i> -oxide
nOe	=	Nuclear Overhauser Effect
Nu (Nuc)	=	nucleophile
P	=	protecting group

Ph	=	phenyl
Piv	=	trimethylacetyl
Piv <sub>2</sub> O	=	trimethylacetic anhydride
PKR	=	Pauson-Khand reaction
ppm	=	parts per million
Pr	=	propyl
<i>i</i> -Pr	=	<i>iso</i> -propyl
<i>p</i> TSA	=	<i>para</i> -toluene sulfonic acid
RBF	=	round-bottom flask
rt (RT)	=	room temperature
s	=	singlet
<i>syn</i>	=	<i>synclinal</i>
t	=	triplet
T	=	temperature
TBS	=	tributylsilyl
TBDMS	=	<i>tert</i> -butyldimethylsilyl
TBDPS	=	<i>tert</i> -butyldiphenylsilyl
<i>tet</i>	=	<i>tetrahedral</i>
Tf	=	trifluoromethanesulfonyl
Tf <sub>2</sub> O	=	trifluoromethanesulfonic anhydride
TFA	=	trifluoroacetic acid
THF	=	tetrahydrofuran
TIPS	=	tri- <i>iso</i> -propylsilyl
TLC	=	Thin Layer Chromatography
TMS	=	trimethylsilyl
TMSD	=	(trimethylsilyl)diazomethane
<i>trig</i>	=	<i>trigonal</i>
Ts	=	<i>para</i> -toluenesulfonate

## 1.0 Introduction

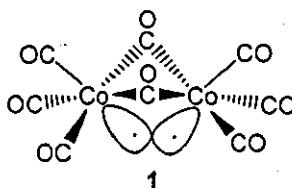
### 1.1 Binary metal carbonyl complexes

The eighteen electron ( $18e^-$ ) rule is obeyed for most low oxidation state transition metals associated with  $\pi$ -acceptor ligands and this is the case with respect to both cobalt and molybdenum carbonyl complexes. Molybdenum is in group six of the periodic table and hence has six valence electrons. To conform to the  $18e^-$  rule it must gain another twelve electrons. As a carbon monoxide ligand donates two electrons, when molybdenum is coupled to six carbon monoxide ligands an  $18e^-$  octahedral complex is created. On reaction with the cyclopentadienyl  $\eta^5$ -ligand, with the loss of three carbon monoxide ligands a seventeen electron complex is created [ $\text{Mo} (6e^-) + \text{Cp} (5e^-) + 3 \times \text{CO} (6e^-)$ ], which is unstable. To increase stability and obey the  $18e^-$  rule complexes of this type tend to dimerise, the molybdenum atoms thus sharing an electron each in a metal-metal bond (**Scheme 1**).



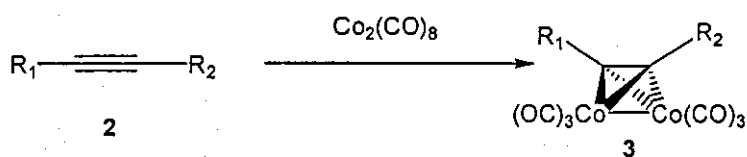
**Scheme 1**

As cobalt is in group nine, it is unable to create a stable metal carbonyl complex with one atom of cobalt. A  $17e^-$  complex is created with four carbon monoxide ligands and  $19e^-$  with five ligands. So in contrast to molybdenum, it forms a dicobalt octacarbonyl metal dimer **1** ( $\text{Co}_2(\text{CO})_8$ ), again with each metal atom donating an electron to create a metal-metal bond. From X-ray crystallographic studies<sup>1</sup> of  $\text{Co}_2(\text{CO})_8$  it was established that two of the carbon monoxide ligands are bridging between the cobalt atoms, each donating one electron to each cobalt centre. This prevents the cobalt-cobalt (Co-Co) bonding orbitals becoming colinear, resulting in a bent Co-Co bond and each of the cobalt centres are  $sp^3d^2$  hybridised, which is consistent with an octahedral environment (**Scheme 2**).



**Scheme 2**

Dicobalt octacarbonyl and molybdenum cyclopentadienyl tricarbonyl dimer both react with alkyne substrates **2** to spontaneously create metal carbonyl complexes **3** on the loss of two carbon monoxide ligands. Each metal centre obeys the 18e<sup>-</sup> rule as the alkyne is counted as a four electron donor, two for each metal centre (**Scheme 3**).



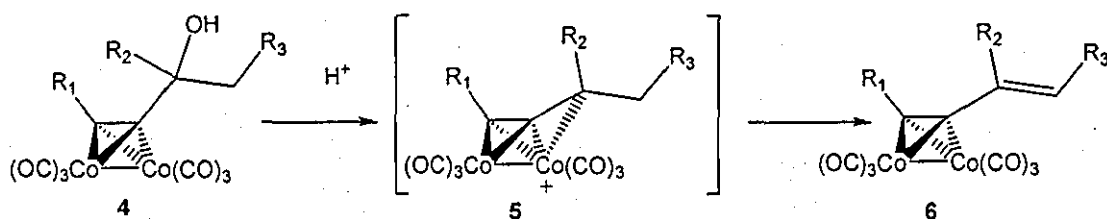
**Scheme 3**

The synthesis and use of bimetallic-alkyne complexes has been well documented in the literature.<sup>2</sup> By far the most frequently reported are those of dicobalt hexacarbonyl-( $\mu$ -alkyne) complexes. Since their discovery in 1956,<sup>3</sup> for use as a protecting group for alkyne functionality in reduction and hydroboration processes,<sup>4</sup> their synthetic utility has expanded notably in favour of its application to the Nicholas<sup>5</sup> and Pauson-Khand reactions respectively.<sup>6</sup>

## 1.2 The Nicholas Reaction

### 1.2.1 Reaction Discovery

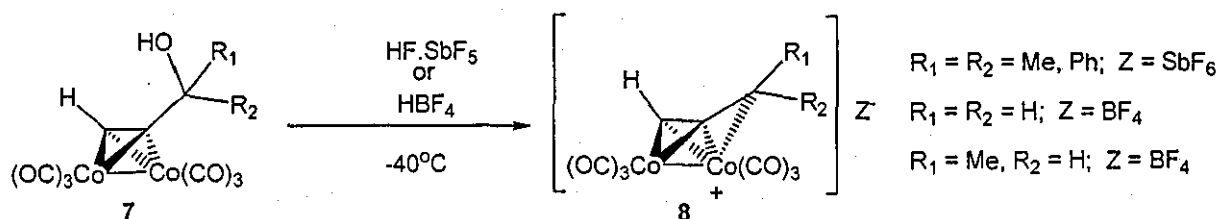
In 1972, Nicholas and Petit first reported the facile acid-catalysed dehydration of dicobalt hexacarbonyl-complexed propargylic alcohols **4**, to the corresponding 1,3-enyne derivatives **6** (Scheme 4). The instability of uncomplexed propargylic alcohols under identical conditions suggested the presence of the stable  $[(\text{propargylum})\text{Co}_2(\text{CO})_6]^+$  cation **5** in complexed systems.<sup>5</sup> A previous report had also shown how identical 1,3-enyne complexes could be hydrated under mildly acidic conditions, further suggesting the stability of a complexed propargylic cation.<sup>4</sup>



Scheme 4

### 1.2.2 Evidence for $[(\text{propargylum})\text{Co}_2(\text{CO})_6]^+$ cations

Further evidence for presence of the  $[(\text{propargylum})\text{Co}_2(\text{CO})_6]^+$  cation intermediate, was demonstrated by Nicholas and Pettit, who were able to isolate and observe these cations by using <sup>1</sup>H NMR spectroscopy at 10°C, after generation by deuterated-TFA.<sup>5</sup> After further research, Connor and Nicholas were able to synthesise salts of these cations. Dark red, stable solids **8** were isolated on reaction of propargyl alcohols **7** with excess tetrafluoroboric acid etherate or HF-SbF<sub>5</sub> (Scheme 5).<sup>7</sup>

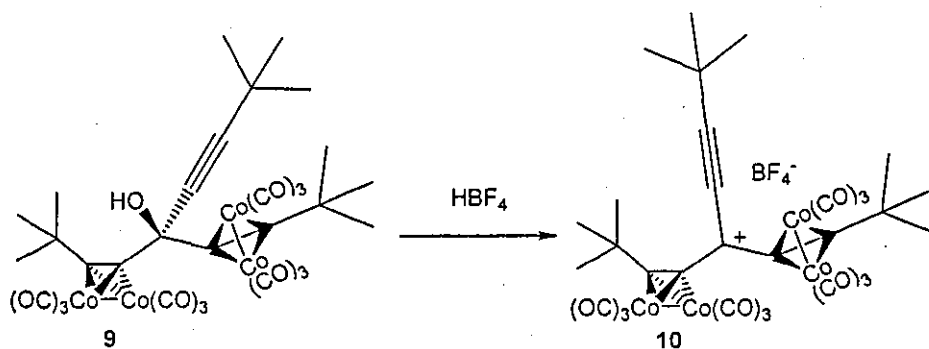


Scheme 5



These reaction intermediates are only isolable due to the high stability created from the considerable delocalisation of the cationic charge onto the cobalt complex. The charge delocalisation is supported experimentally by a 40-60  $\text{cm}^{-1}$  increase in the IR absorption frequencies of the  $\text{C}\equiv\text{O}$  ligands present in the cations, in comparison with those in the parent alcohols. The magnitude of this increase is consistent with greater C-O bonding, resulting from a decreased  $d(\text{Co}) \rightarrow \pi^*(\text{CO})$  donation from the cobalt in the electron-deficient cations.  $^1\text{H}$  NMR evidence shows alkyl groups  $\alpha$  to the cationic centre experience smaller deshielding effects relative to neutral complexes. This is supported by  $^{13}\text{C}$  NMR showing resonances for the co-ordinated  $\text{C}\equiv\text{C}-\text{C}$  system and  $\text{C}\equiv\text{O}$  ligands expressing small shielding effects.

The first X-ray crystal structure of a  $[(\text{propargylium})\text{Co}_2(\text{CO})_6]^+$  cation was recently published by Melikyan et al.<sup>8</sup> The compound **10** chosen for the study contained two stabilising  $\text{Co}_2(\text{CO})_6$  groups, creating increased stability and crystallinity of the cation (Scheme 6).

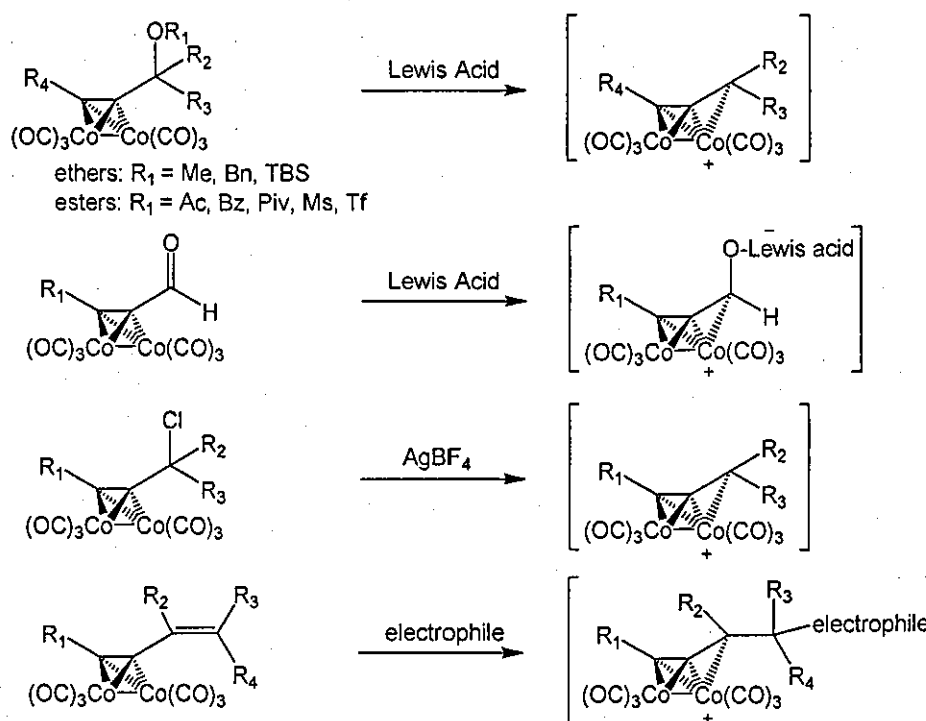


Scheme 6

On comparison of the two crystal structures, generation of the  $\text{sp}^2$  cation **10**, leads to a trigonal planar arrangement of atoms, in contrast to the tetrahedral arrangement in **9**. The covalent bonds around the central carbon all shorten in the cation, due to the increased  $s$ -character in the hybridisation of their orbitals. A shift of the central carbon atom towards one of the cobalt centres in each pair is evident in **10**, contrasting with it sitting equidistant in **9**, and this further illustrates the physical changes that result from carbocationic charge stabilisation by the metal centres.

### 1.2.3 Generation of [(propargylium)Co<sub>2</sub>(CO)<sub>6</sub>]<sup>+</sup> cations

Stabilised [(propargylium)Co<sub>2</sub>(CO)<sub>6</sub>]<sup>+</sup> cations can be generated by a variety of methods (Scheme 7). The most frequently used is the protonation of the parent alcohol, as seen above (Scheme 6). Treatment of complexed propargyl ethers, esters or aldehydes with Lewis acids, all produce the required carbocations *in situ* preceding further reaction with nucleophiles. A wide range of different ethers can be utilised, including many alkyl, benzyl and silyl derivatives.<sup>9</sup> Acetate, benzoate and pivalate esters can also be used, along with sulfonic acid esters such as mesylates<sup>10</sup> or triflates.<sup>11</sup> Silver tetrafluoroborate used in conjunction with a suitable propargyl chloride<sup>12</sup> and electrophilic addition to 1,3-enyne complexes, are further routes of producing these carbocations.<sup>13</sup>

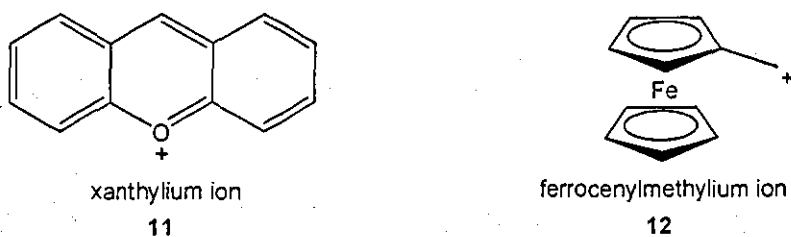


Scheme 7

### 1.2.4 Nucleophilicity of [(propargylium)Co<sub>2</sub>(CO)<sub>6</sub>]<sup>+</sup> cations

Cobalt stabilised carbocations react with a wide variety of nucleophiles, making them extremely versatile substrates. Mayr et al.<sup>14</sup> have investigated the kinetics of several

reactions involving simple  $[(\text{propargylium})\text{Co}_2(\text{CO})_6]^+$  cations with a host of different  $\pi$ -nucleophiles and hydride donors. From their studies, they were able to categorise and rank the cobalt-stabilised propargyl cations in terms of their electrophilicity parameters, relative to other known electrophiles. Mayr et al. concluded that  $[(\text{propargylium})\text{Co}_2(\text{CO})_6]^+$  cations behave in a similar manner to the xanthylum 11 and ferrocenylmethylium 12 ions (Scheme 8).



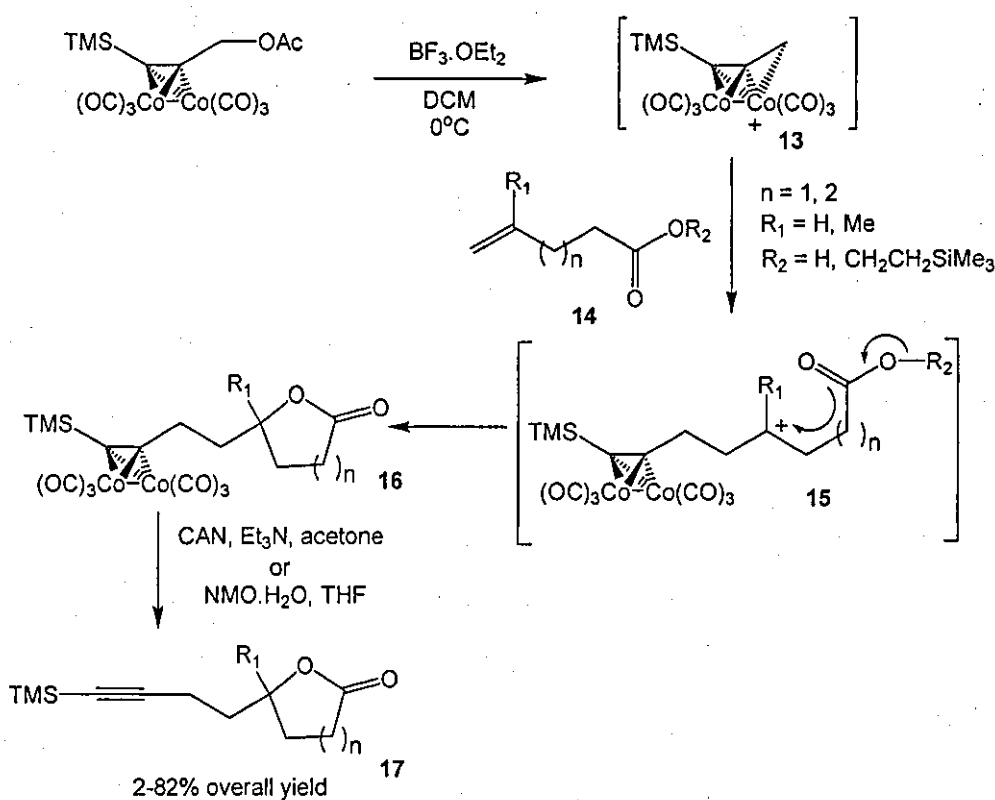
**Scheme 8**

These results allow predictions of which nucleophiles  $[(\text{propargylium})\text{Co}_2(\text{CO})_6]^+$  cations should react with. Suitable substrates include alkenes, allylsilanes, electron rich aromatics, allylstannanes, enol ethers and silyketene acetals, which is in good agreement with examples in the literature.

### 1.3 Reaction with carbon nucleophiles

#### 1.3.1 Alkene Nucleophiles

The first use of parent alkene nucleophiles was carried out by Krafft et al.<sup>15</sup> on reacting [(propargylium)Co<sub>2</sub>(CO)<sub>6</sub>]<sup>+</sup> cations **13** with the terminal alkenyl acid and ester **14** (Scheme 9). The resulting carbocation **15** then reacted in an intramolecular fashion with the acid/ester to give a lactone **16**, which was finally decomplexed to give **17** in poor to very good yield. Optimum yields were created on formation of five-membered lactones (n=1) and for tertiary carbocations (R<sub>1</sub>=Me).

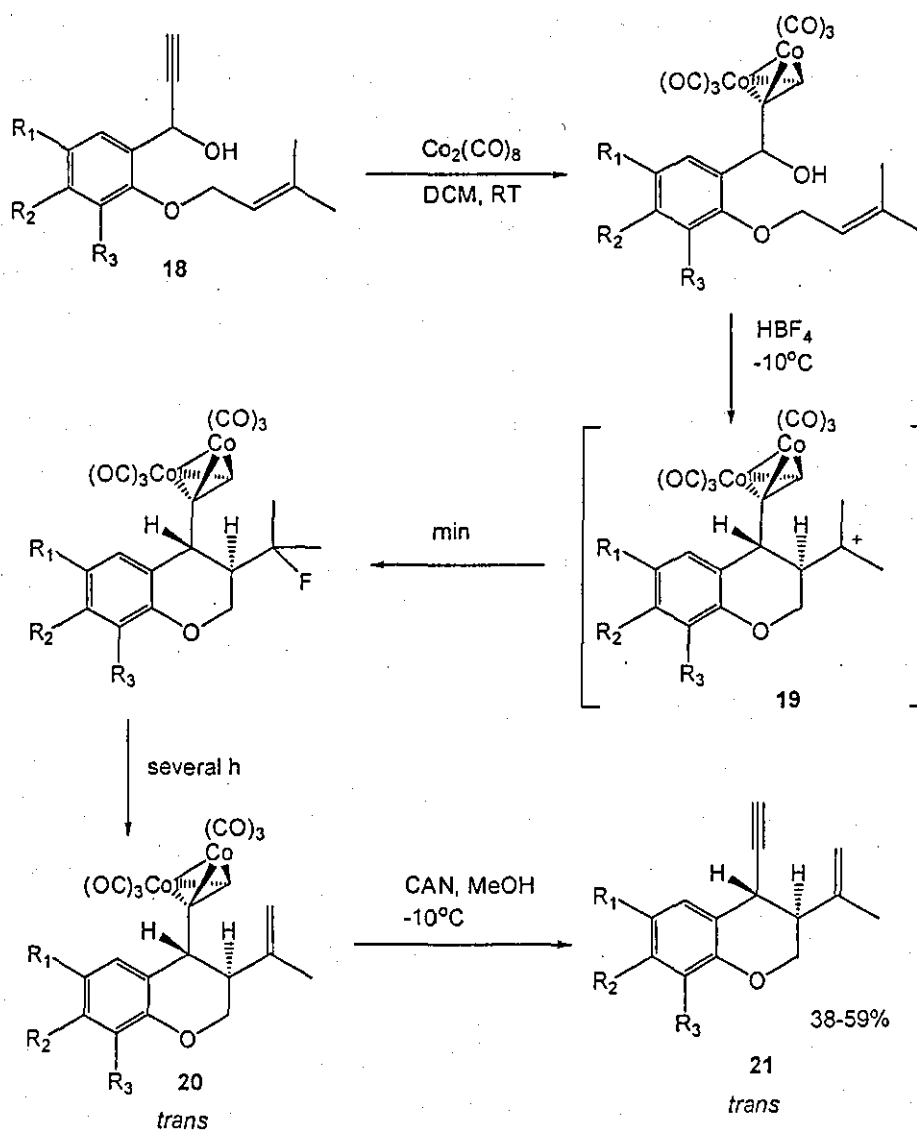


Scheme 9

Tethered trisubstituted alkene nucleophiles have also been investigated by Tyrrell et al.<sup>16, 17</sup> who carried out a ring closure onto a benzylic Nicholas cation, during a one-pot synthesis of benzopyrans (Scheme 10). Initially, propynol **18** was complexed with  $\text{Co}_2(\text{CO})_8$ , before cyclisation using  $\text{HBF}_4$ . The intermediate carbocation **19**, produced after the cyclisation was quenched by a fluoride anion after treatment with tetrafluoroboric acid. On allowing the reaction mixture to stand for several hours the

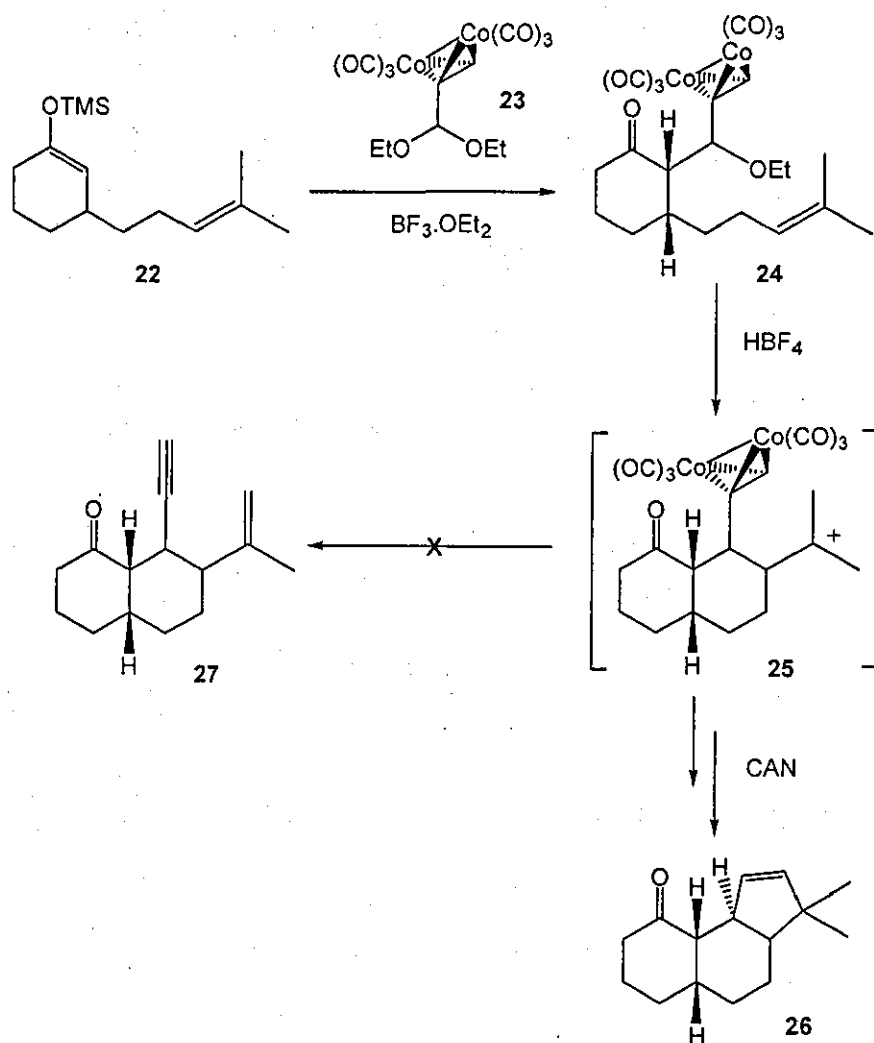
several hours the de-halogenated alkene **20** is fashioned *via* loss of HF. Finally on addition of CAN, *trans*-isopropenyl benzopyrans **21** were created in moderate to good overall yield, with degree of substitution on the alkene being the major factor in the variation of yield.

Disubstituted alkenes failed to cyclise under these conditions, reinforcing the findings of Krafft et al.<sup>15</sup> suggesting that yields are drastically reduced when generating secondary rather than tertiary carbocations after cyclisation, alongside the decreased nucleophilicity of disubstituted alkenes.



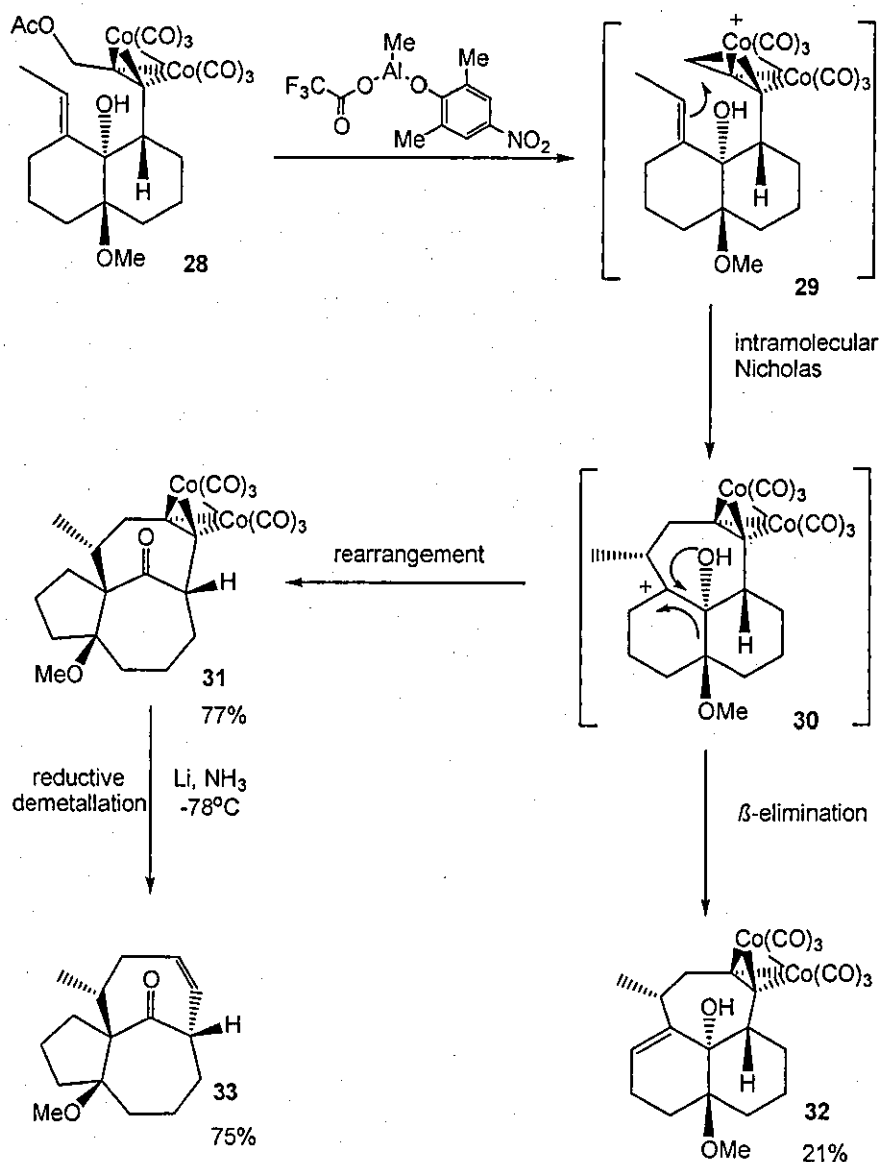
Scheme 10

Tyrrell et al. wanted to extend this methodology towards the cyclisation of non-aromatic precursors,<sup>18</sup> therefore attempts were made to create substituted decalins. However, instead of producing the desired decalin product, the reaction resulted in a *cis-anti-trans* tricycle being formed (**Scheme 11**). In a further one-pot procedure, the Nicholas complex **23** was reacted with the silyl enol ether **22** to form the *cis*-precursor **24**. Upon treatment with hydrofluoroboric acid, cyclisation took place. Presuming the tertiary carbocation **25** is created, a further cyclisation to form the unexpected tricycle **26** occurs, which was isolated after treatment with CAN in a moderate overall yield. Even on using a series of other decomplexation methods, no decalone **27** could be isolated.



**Scheme 11**

In an effort to synthesise the highly strained ingenane skeleton whilst working towards the total synthesis of ingenol, Tanino et al.<sup>19, 20</sup> developed a tandem Nicholas cyclisation-rearrangement strategy (**Scheme 12**).



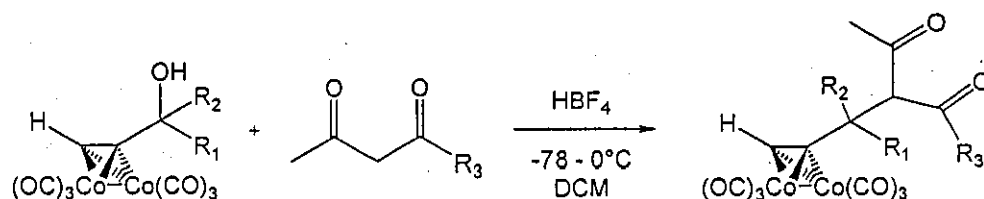
**Scheme 12**

Upon treatment with suitably substituted aluminium Lewis acids, the cobalt complex **28** formed a **[(propargylium)Co<sub>2</sub>(CO)<sub>6</sub>]<sup>+</sup>** cation **29**, which could then be trapped with the adjacent alkene to form the tertiary carbocation **30**. A pinacol-type rearrangement then took place to yield the ingenane core **31**, in 77% yield, with 21% of the allyl alcohol **32** also produced from a  $\beta$ -hydride elimination side reaction. The cobalt

complex was cleaved reductively under Birch conditions to give the alkene product **33**, in 75% yield.

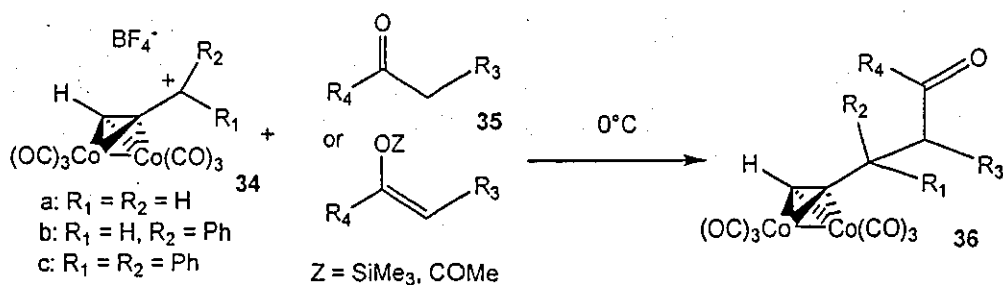
### 1.3.2 Enolate Nucleophiles

The first report of an enolate addition to a  $[(\text{propargylium})\text{Co}_2(\text{CO})_6]^+$  cation was on the selective propargylation of  $\beta$ -dicarbonyl compounds by Nicholas and Hodes<sup>21</sup> (Scheme 13). The reaction of acetylacetone and benzoylacetone with a propargylic cation generated *in situ* on treatment with hydrofluoroboric acid, created the alkylated products generally existing in their dicarbonyl tautomer (> 95% by NMR spectroscopy) in good to high yield, with no sign of any allenic by-products. When  $R_2$  and  $R_3$  were phenyl the new asymmetric centre was formed in a 93:7 ratio of diastereoisomers, when quenching after only a few minutes to yield an excess of the kinetic product.



Scheme 13

Nicholas further extended this methodology by regiospecifically reacting the  $[(\text{propargylium})\text{Co}_2(\text{CO})_6]^+$  cation with ketones, silyl enol ethers and enol acetates (Scheme 14).<sup>22</sup>

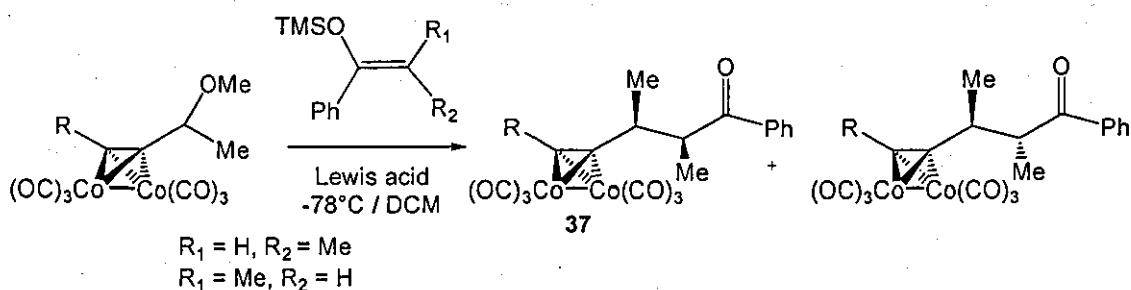


Scheme 14



The propargylic cation **34**, was dissolved in excess dry ketone **35** at 0°C and rapid reaction (30-90 min) produced exclusively the  $\alpha$ -monoalkylated product **36** in generally high yield. When reacting with unsymmetrical ketones a high regioselectivity was seen, giving the most thermodynamically favoured product. The degree of selectivity was exceptional ( $\geq 95\%$ ), on comparison with other acid-catalysed  $\alpha$ -substitution reactions. As a large excess of ketone was needed to maintain high yields, Nicholas moved onto the reaction of silyl enol ethers and enol acetates. Reaction of equimolar quantities of cation salts and enol derivatives in DCM at 0°C (30-60 min) produced the monoalkylated products in moderate to excellent yield.

Schreiber et al. developed the first stereoselective enolate addition to the  $[(\text{propargylium})\text{Co}_2(\text{CO})_6]^+$  cation, with a Lewis acid mediated synthesis of *syn*-alkylated molecules (**Scheme 15**).<sup>23</sup>



**Scheme 15**

The reaction of both (*E*)- and (*Z*)-trimethylsilyl enol ethers of propiophenone, resulted in synthesis of predominately the *syn* diastereoisomer **37**. As with the aldol reaction, the (*Z*)-enol ether provided higher levels of diastereoselection. Upon changing R from H to SiMe<sub>3</sub>, the d.r. increased from 1.6:1, to 15:1. The rationale for this stereoselectivity, is based on a transition state with a *synclinal* alignment of the two  $\pi$ -systems, where the two methyl groups are antiperiplanar to the  $\pi$ -systems, thus resulting in *syn*-alkylated products. This helps to explain the role of substituent R, with minimised van der Waals strain between the methyl group and enol ether (**Figure 1**).

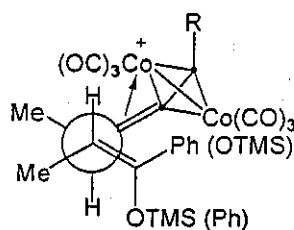
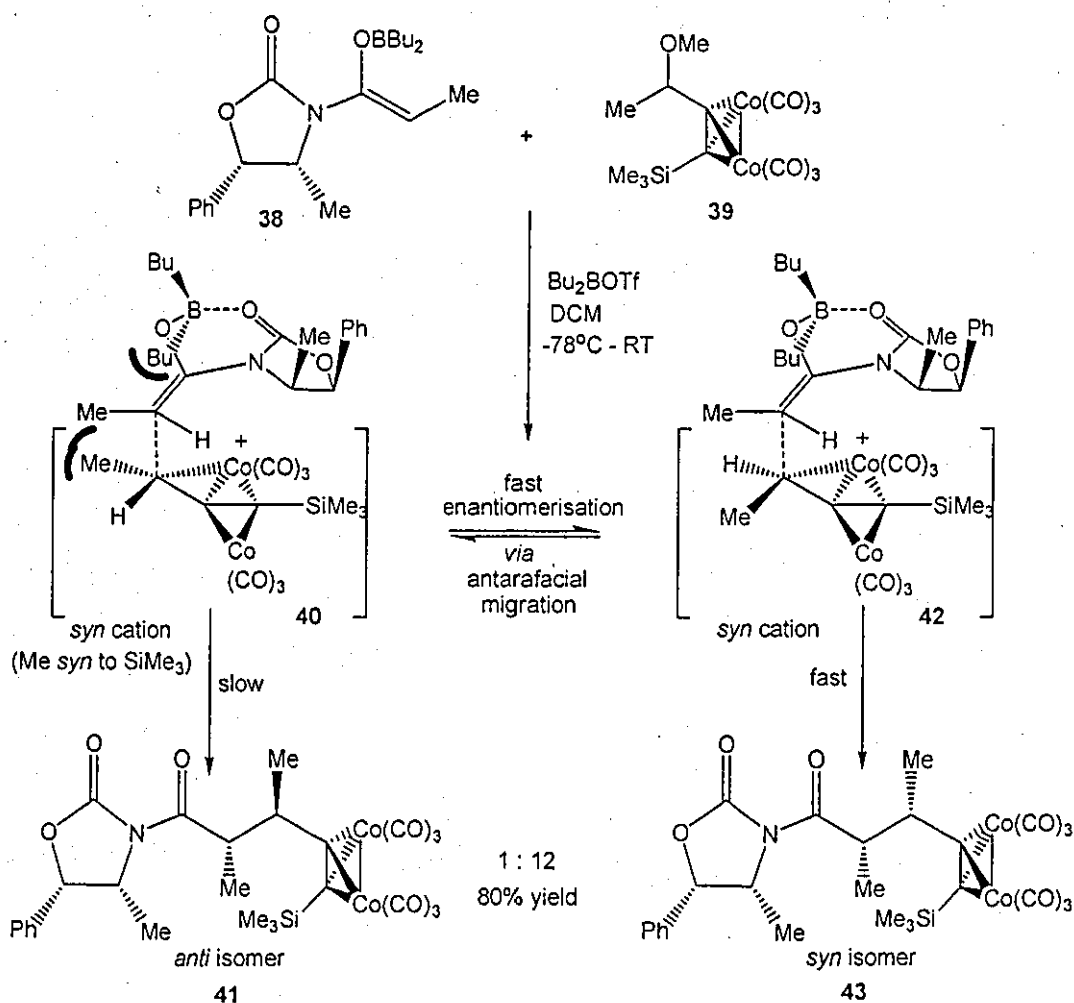


Figure 1

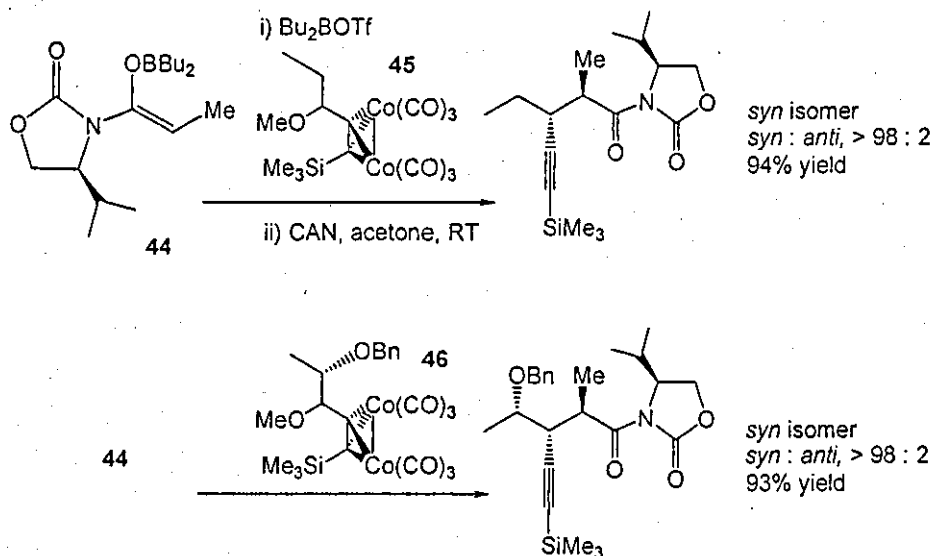
Schreiber et al.<sup>24</sup> followed up this work by using boron enolates, derived from the Evans chiral oxazolidinone as nucleophiles. Upon reaction with [(propargylium)Co<sub>2</sub>(CO)<sub>6</sub>]<sup>+</sup> cations, chiral products were provided in good yield. Addition of the chiral enolate **38** with the cobalt complex **39**, resulted in a chiral 12:1 mixture of the *syn:anti* products **43** and **41** respectively, in 80% yield (Scheme 16).



Scheme 16

Schreiber accounted for this result by suggesting a novel double stereodifferentiating process, where the cobalt stabilised cation rapidly interconverts *via* enantiomerisation at a faster rate than the competing alkylation reaction. By considering the Seebach *synclinal* transition state,<sup>25</sup> if a *syn* enantiomer (Me *syn* to SiMe<sub>3</sub>) approaches the chiral enolate, the cation would react to give the *anti* alkylation product. However this reaction pathway is sterically hindered, due to a steric interaction between the methyl group and one of the butyl groups on the boron enolate. The *syn* cation does not experience the same steric effect, therefore this reaction is faster. NMR analysis by Schreiber et al.<sup>24</sup> showed how cobalt stabilised cations e.g. 40 and 42 rapidly undergo interconversion. This interconversion occurs *via* an antarafacial migration, and if the migration rate is faster than the corresponding alkylation reaction, the cation will convert and react to generate the *syn* product in preference.

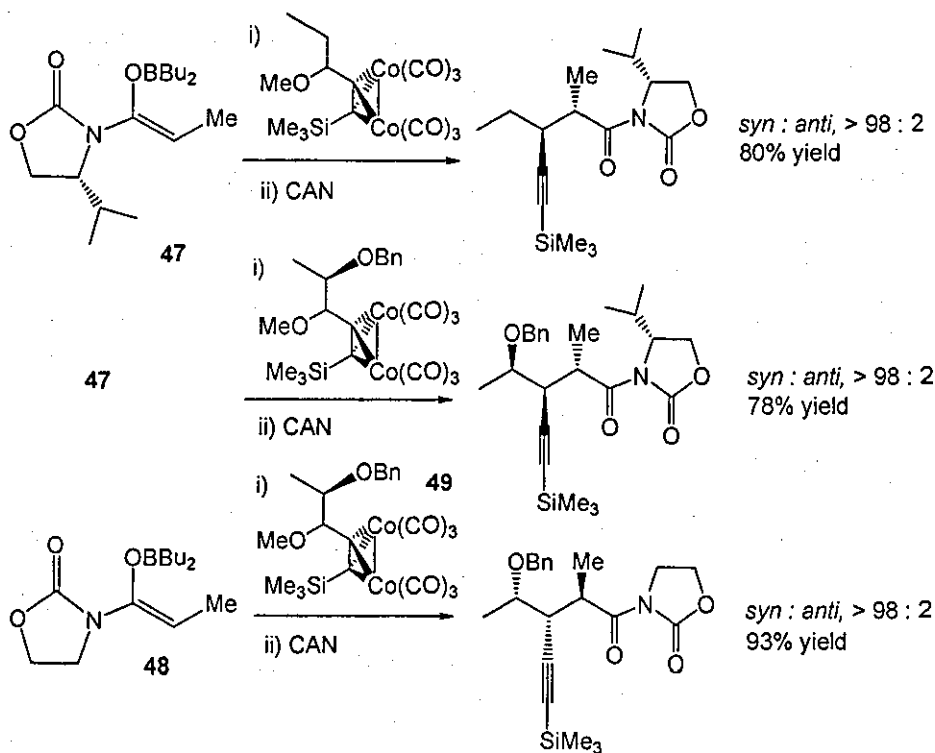
In the early 90's, Jacobi and co-workers<sup>26-32</sup> used a host of chiral and non-chiral boron oxazolidinone enolates e.g. 44 to alkylate a variety of dicobalt hexacarbonyl stabilised cations e.g. 45 and 46, many of them containing chiral substituents (Scheme 17).



Scheme 17

The chiral products were then used to prepare intermediates in the synthesis of tetrapyrrole and  $\beta$ -lactam systems. The majority of enolate and cation pair examples appear to be 'matched' resulting in high levels of diastereo- and enantioselective

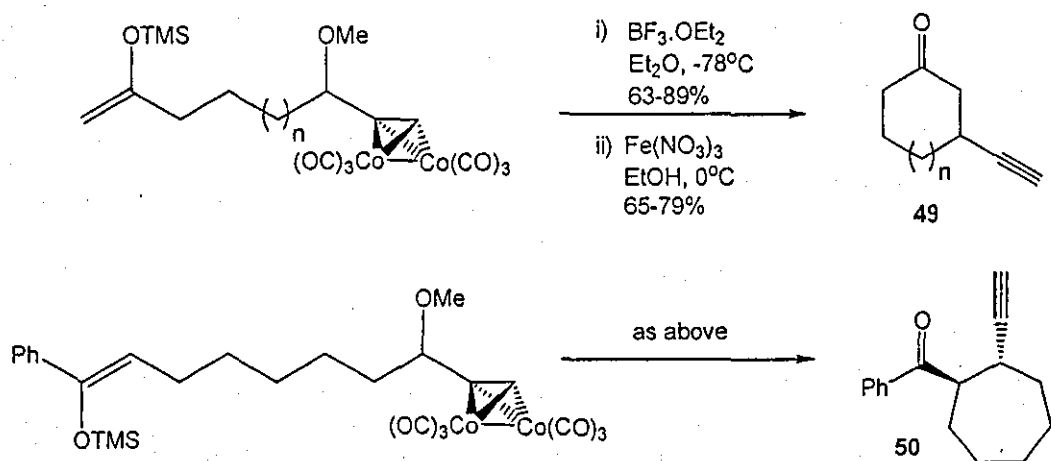
control, with *syn:anti* ratios of > 98:2 being achieved. Remarkably, even the chirality of the  $[(\text{propargylium})\text{Co}_2(\text{CO})_6]^+$  alone could control the selectivity of the reaction, as seen in the excellent diastereo- and enantioselectivity in the reaction between the cation of the benzyl ether **49** and the achiral enolate **48** (Scheme 18).



**Scheme 18**

If however, the enolate and cation are ‘mismatched’, then in the transition state the chirality of the enolate will interfere with the chirality of the cation, resulting in poor yields and selectivities. The reaction can even yield an excess of the unfavoured *anti* isomer, in a complete reversal of stereoselectivity. Further research has yet to be carried out to precisely determine which enolate/cation pairings will be ‘matched’ or ‘mismatched’. At present there appears to be no accurate transition state model to predict this.

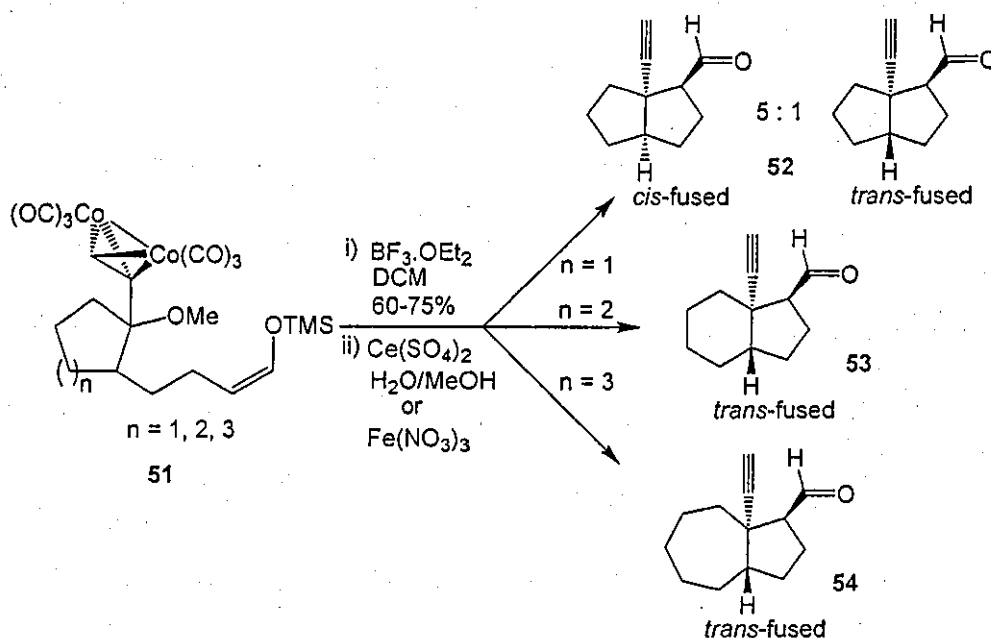
In an effort to synthesise cyclic  $\beta$ -alkynyl ketones, Tyrrell et al.<sup>33</sup> investigated the intramolecular reaction between silyl enol ethers and  $[(\text{propargylium})\text{Co}_2(\text{CO})_6]^+$  carbocations (Scheme 19).



Scheme 19

Depending upon the enol ether substrate used, the resulting keto product can be either *endo*- 49 or *exo*-cyclic 50. In agreement with the transition state model as described by Schreiber,<sup>23</sup> for *exo*-cyclic keto groups to be created a *trans* stereochemistry is required.

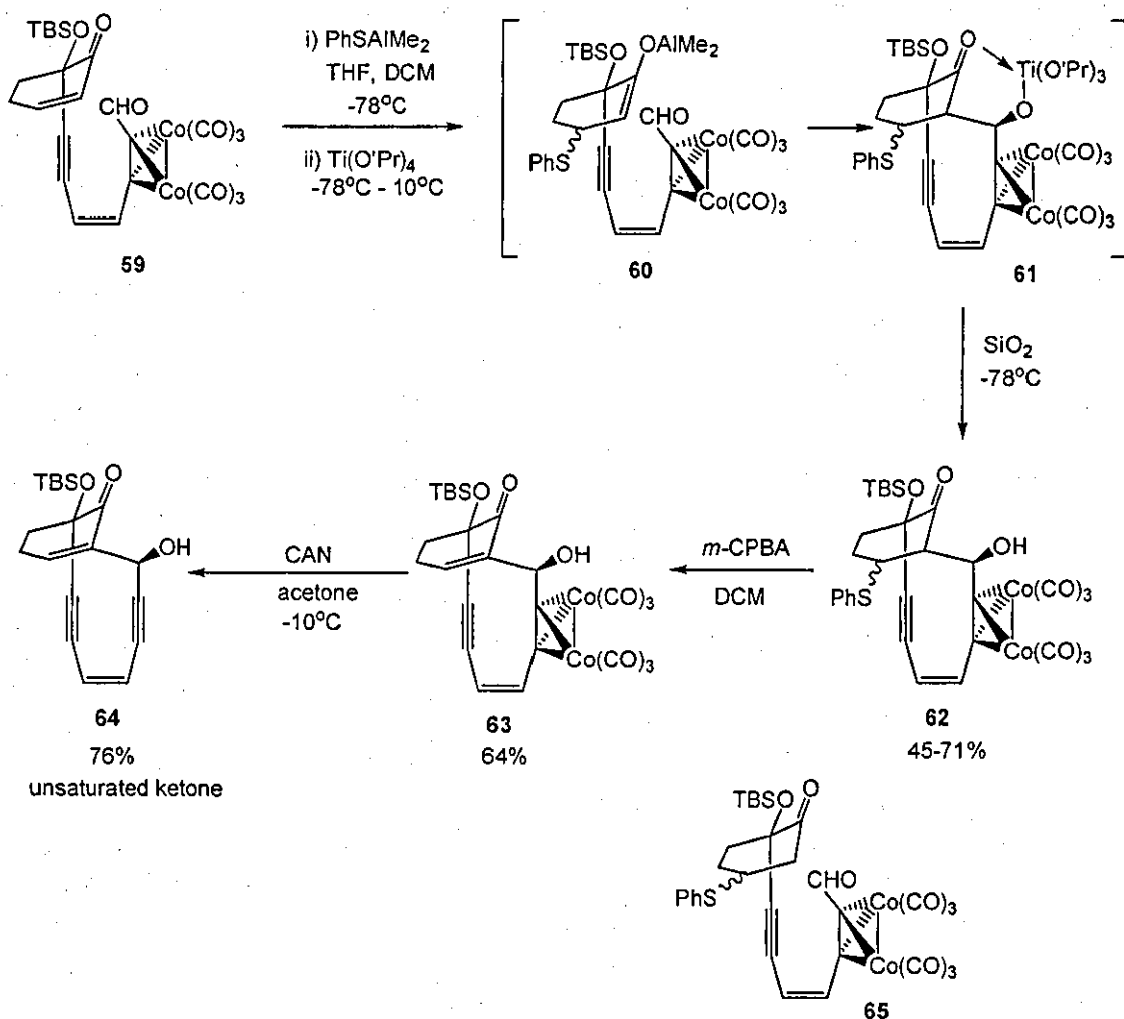
Tyrrell<sup>34</sup> extended the scope of this area to the synthesis of bicyclic rings (Scheme 20). Upon treatment with boron trifluoride etherate, the cyclopentane derivative 51 ( $n=1$ ), cyclised to form the unstable *cis*-fused:*trans*-fused bicyclic aldehyde 52 in a 5:1 mixture of diastereoisomers, after decomplexation. In contrast, on cyclisation of larger cyclohexane 51 ( $n=2$ ) and cycloheptane 51 ( $n=3$ ) derivatives, *trans*-fused bicyclic aldehydes 52 and 54 were fashioned exclusively. As reported previously, the relationship between the pendant aldehyde and alkyne moiety on the created ring is *trans* in each case.



Scheme 20

Montaña et al.<sup>35, 36</sup> utilised the Nicholas reaction in their seven step synthesis of the *trans*-fused bicyclo[5.3.0]decane ring **58** (Scheme 21). Nucleophilic attack of the silyl enol ether **56** onto the [(propargylium) $\text{Co}_2(\text{CO})_6$ ]<sup>+</sup> carbocation, derived from the acetal **55**, inserted a  $\text{C}_3$  subunit which eventually becomes the five-membered ring fragment **58**. The large size of the cobalt group ensures that the attack is directed exclusively at the *exo* face of the silyl enol ether, resulting in the formation of a single isomer at the centre of attachment. Oxidation of the metal complex allowed access to the alkyne **57**, which could then be further transformed to **58** after a series of steps.



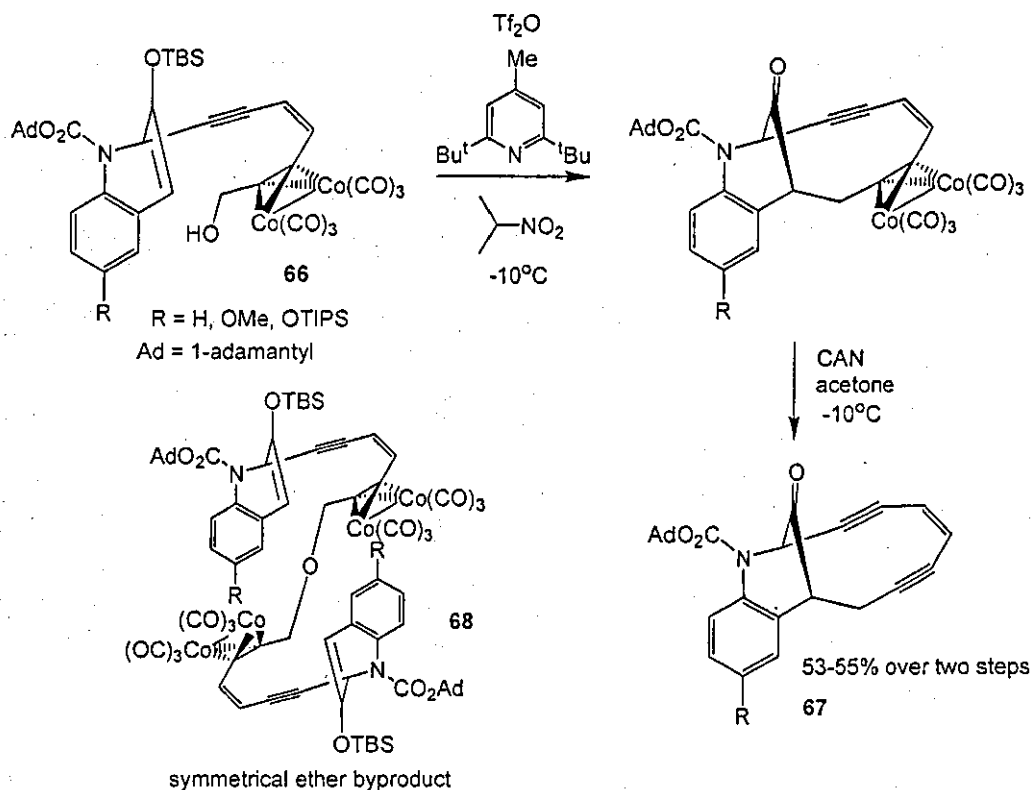


Scheme 22

Starting with the cobalt complex **59**, two diastereomeric  $\beta$ -sulfides, most likely **60** were obtained on addition of  $\text{PhSAI}(\text{Me})_2$ . Only one of these  $\beta$ -sulfides cyclises on addition of titanium tetrakisopropoxide to form compound **61** and the cyclised sulfide is then quenched with silica gel at  $-78^\circ\text{C}$  to prevent any formation of the retro-aldol product **65**. The unstable sulfide **62** is then rapidly oxidised and eliminated to give the stable unsaturated ketone **63**, subsequently decomplexing with  $\text{CAN}$  to give the bicyclo[7.3.1]tridecadienediyn ring product **64**. This route supersedes earlier work by Magnus et al. again using an aldol cyclisation in the synthesis of a bicyclo[7.3.1]tridecadienediyn ring skeleton on addition of dibutylboron triflate/DABCO.<sup>38</sup> Cyclisations involving the use of titanium tetrachloride/DABCO or triflic anhydride/2,6-di-*tert*-butyl-4-methylpyridine with silyl enol ethers have also been reported.<sup>39-41</sup>



Magnus et al.<sup>42</sup> again utilised reaction of a  $[(\text{propargylium})\text{Co}_2(\text{CO})_6]^+$  carbocation with a silyl enol ether in the elegant synthesis of 10-azabicyclo[7.3.1]tridecaenediyne ring system, as found in dynemicin A (Scheme 23).

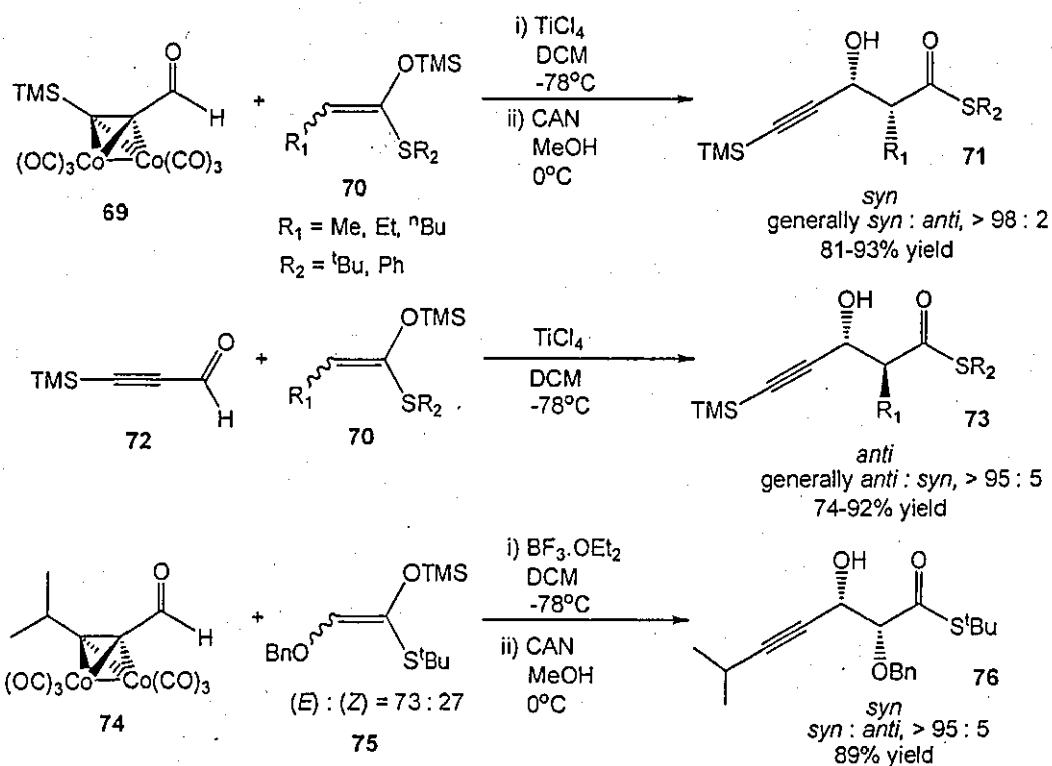


Scheme 23

The stabilised carbocation, generated using triflic anhydride, 2,6-di-*tert*-butyl-4-methylpyridine and 2-nitropropane as solvent, was trapped intramolecularly with a silyl enol ether. In initial trials, using dichloromethane as a solvent, only a symmetrical ether by-product 68 was formed. This outcome was rationalised because dichloromethane is a non-polar, poorly solvating solvent. Therefore the alcohol can hydrogen bond with itself intermolecularly. An immediate reaction with a neighbouring molecule of 66 occurs on generation of the Nicholas carbocation. In order to achieve the desired reaction product, a more polar, enhanced solvating environment was used to help stabilise the propargyl cation long enough to react with the silyl enol ether. 2-Nitropropane was chosen as it exhibits the suitable characteristics required, the desired unstable azabicyclo[7.3.1]tridecaenediyne ring 67 could then be isolated successfully after decomplexation with CAN. A review on the use of  $[(\text{propargylium})\text{Co}_2(\text{CO})_6]^+$

carbocations and the Nicholas reaction, as a general strategy in the synthesis of enediyne antibiotics was published by Magnus in 1994.<sup>43</sup>

Hanaoka and co-workers<sup>44-46</sup> had previously reported that the aldol reaction between propargyl complex **69** and *O*-silylketene *O,S*-acetals **70**, in the presence of titanium tetrachloride gives the *syn* diastereomeric product **71** exclusively. Conversely, the uncomplexed alkyne equivalent **72** reacts under the same conditions to give the *anti* diastereoisomer **73** (Scheme 24).

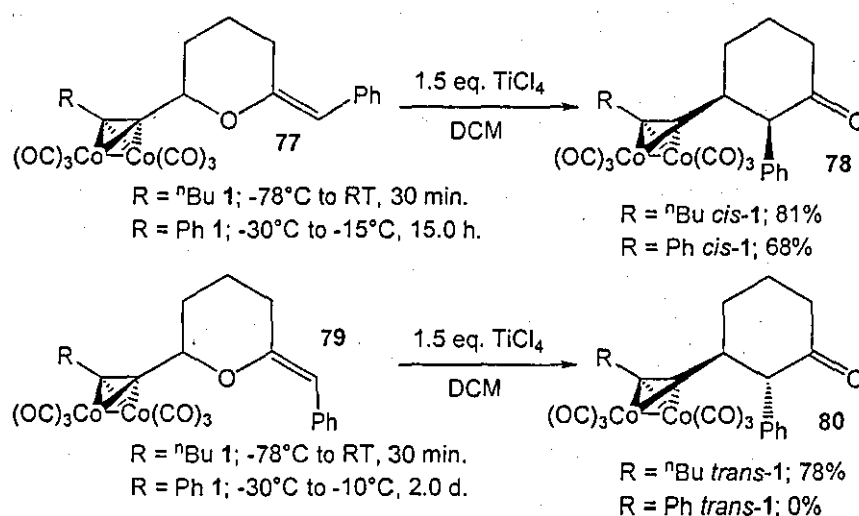


Scheme 24

Hanaoka et al. discovered that both the (*E*)- and (*Z*)-isomers of the *O*-silylketenes *O,S*-acetals react in a stereoconvergent manner to give the same isomeric product in generally very high stereoselectivity. Therefore the stereochemistry of these *O*-silylketenes *O,S*-acetals does not affect the end product. During his development towards the total synthesis of bengamide E, Hanaoka<sup>47-48</sup> showed that the isopropyl-substituted cobalt complex **74**, reacted in the same way with *O*-silylketenes *O,S*-acetals **75** carrying an extra oxygen substituent. The yield was greatly improved on altering the

titanium based Lewis acid, to boron trifluoride etherate, giving the *syn* compound 76 in 89% yield and 95:5 stereoselectivity.

During a stereocontrolled approach to  $\alpha$ -alkyl  $\beta$ -alkynyl cyclohexanones, Harrity et al.<sup>49, 50</sup> investigated the cobalt-mediated stereoselective intramolecular rearrangement of enol ethers to  $\alpha$ -alkyl  $\beta$ -alkynyl cyclohexanones under Lewis acid conditions (Scheme 25).

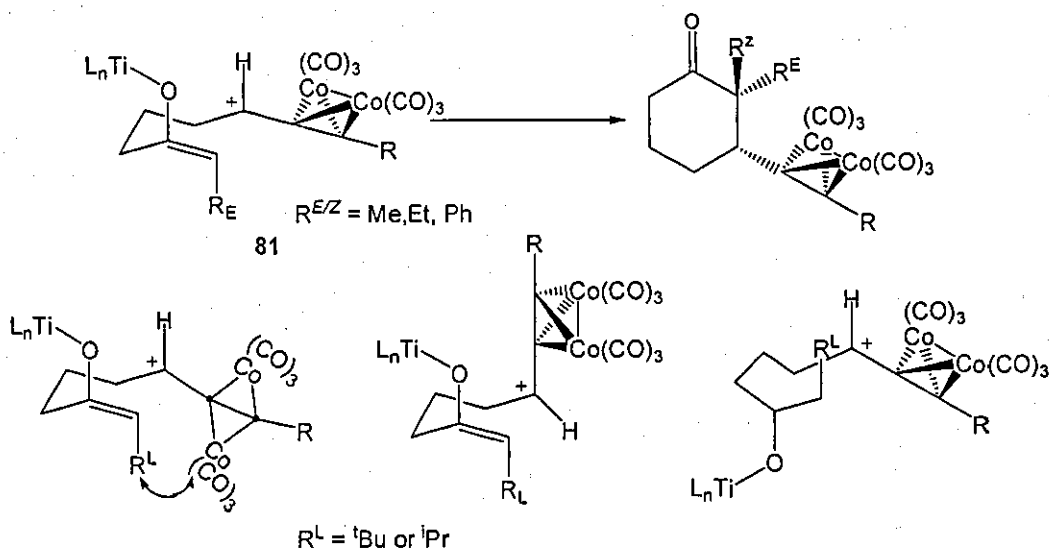


Scheme 25

The titanium promoted rearrangement of enol ethers bearing relatively small alkyl groups (Me, Et, Ph) created the *cis* or *trans* ketone product in a stereoselective manner. (*E*)-Enol ether substrates e.g. 77 are converted to *cis*-disubstituted ketones e.g. 78 and (*Z*)-enol ethers e.g. 79 to *trans*-disubstituted ketones e.g. 80. In contrast, sterically larger enol ethers such as *tert*-butyl derivatives show an opposite trend, in which the (*E*)-enol ether substrate is converted to the *trans*-disubstituted ketone. Substrates which are problematic on using TiCl<sub>4</sub> worked well with Bu<sub>2</sub>BOTf as a Lewis acid mediator, although they were prone to epimerisation to the thermodynamically more stable *trans* diastereoisomer at higher temperatures.

Harrity suggested that titanium mediated rearrangements bearing smaller alkyl groups, react *via* a chair transition state 81 (Figure 2). In the case of the larger *tert*-butyl derivative a different transition state was suggested, due to steric interactions between

the cobalt metal centre and the *tert*-butyl group in a chair conformation. A 180° rotation of the propargylic carbon would reduce the steric clash of these groups and this alternative chair transition state could be operating. This postulate was reinforced by analysis of the crystal structure, which showed how the cobalt metal centre and the *tert*-butyl group are orientated in diaxial positions in a chair conformation. Also, if a boatlike transition state is created, the cobalt complex lies in a pseudoequatorial position, which would be more favourable.

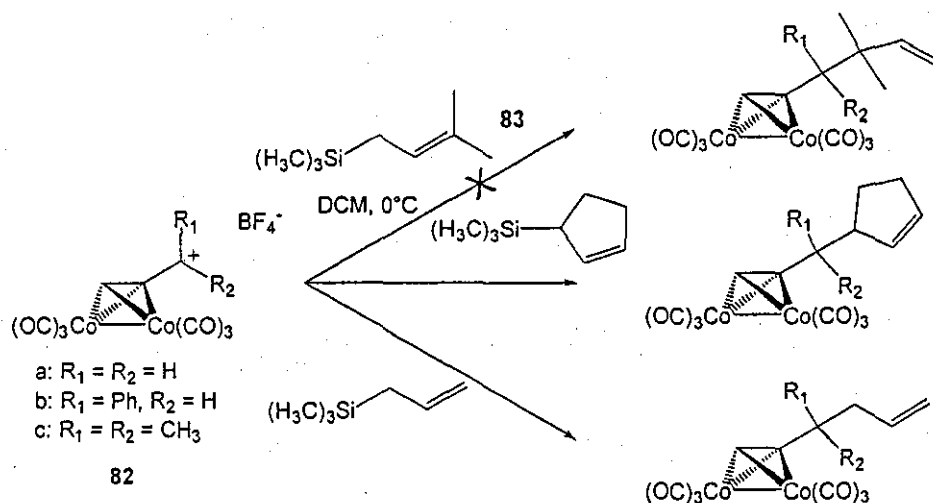


**Figure 2**

### 1.3.3 Allyl Nucleophiles

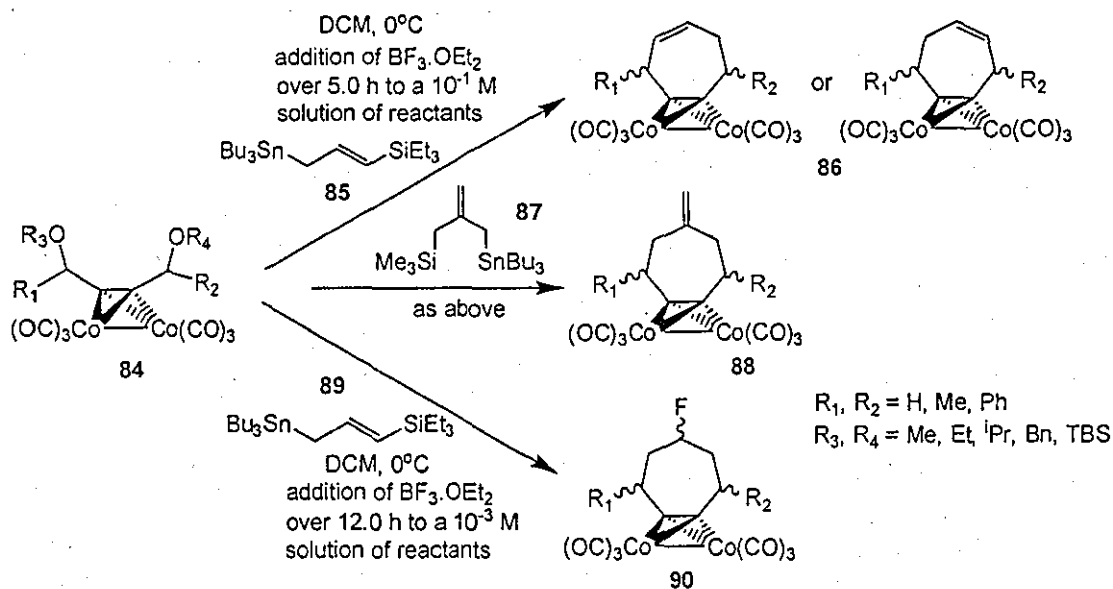
In an effort to selectively create 1,5-enynes as intermediates in the synthesis of acyclic isoprenoids, Nicholas coupled propargylic complexes **82** with allyl silanes (**Scheme 26**).<sup>51</sup>

Allyl silanes were reacted with propargylic Nicholas salt complexes in DCM at 0°C. A wide range of 1,5-enynes were generally isolated in good to excellent yield, and only on addition of 3,3-dimethylallyl silane **83** to the tertiary propargylic cation **82** did no reaction occur.



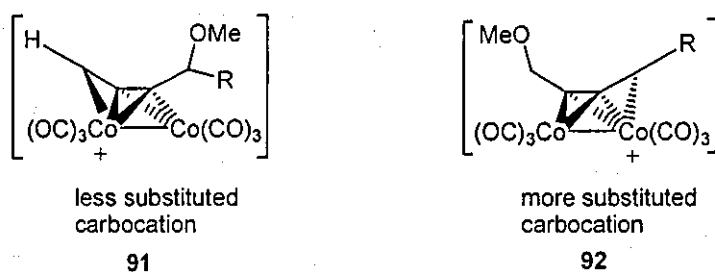
Scheme 26

Green successfully employed a double Nicholas reaction involving alkynyl diether complexes **84** with allyldimethyls 85, 87, 89 in his synthesis of cobalt complexed cycloheptyne derivatives **86**, **88**, **90** (Scheme 27).<sup>52</sup>



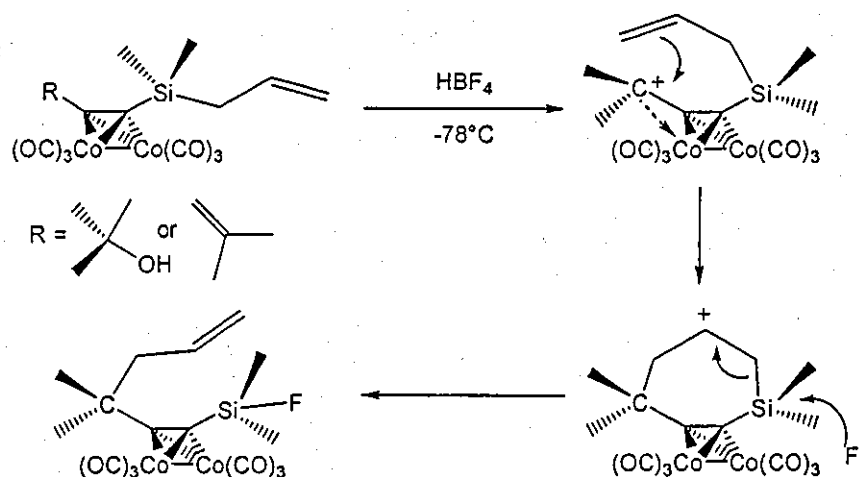
Scheme 27

Green discovered that on slow addition of a Lewis acid to a solution of silylstannane and the diether complex at 0°C, the desired cycloheptane derivatives **86** and **88** could be isolated in moderate to good yields. By changing the substituent groups R<sub>1</sub>-R<sub>4</sub>, it was shown that the double bond regiochemistry of the product was set up by the formation of the less substituted carbocation, therefore **91** forms in preference over **92** (Figure 3) and formation of the *trans* diastereoisomer of the product predominates over the *cis* diastereoisomer. Surprisingly, by a much slower addition of the Lewis acid into a more dilute solution of reactants, a fluoride product **90** was fashioned in 55-80% yield.



**Figure 3**

Intramolecular allyl transfer from silicon onto a [(propargylium)Co<sub>2</sub>(CO)<sub>6</sub>]<sup>+</sup> cation was achieved by McGlinchey et al.<sup>53</sup> (Scheme 28). Migration proceeds readily with concomitant formation of the thermodynamically favoured Si-F bond, most likely *via* a seven-membered ring pathway involving a β-silyl cation. Precedent for this proposal has been reported by Green.<sup>23, 52</sup>

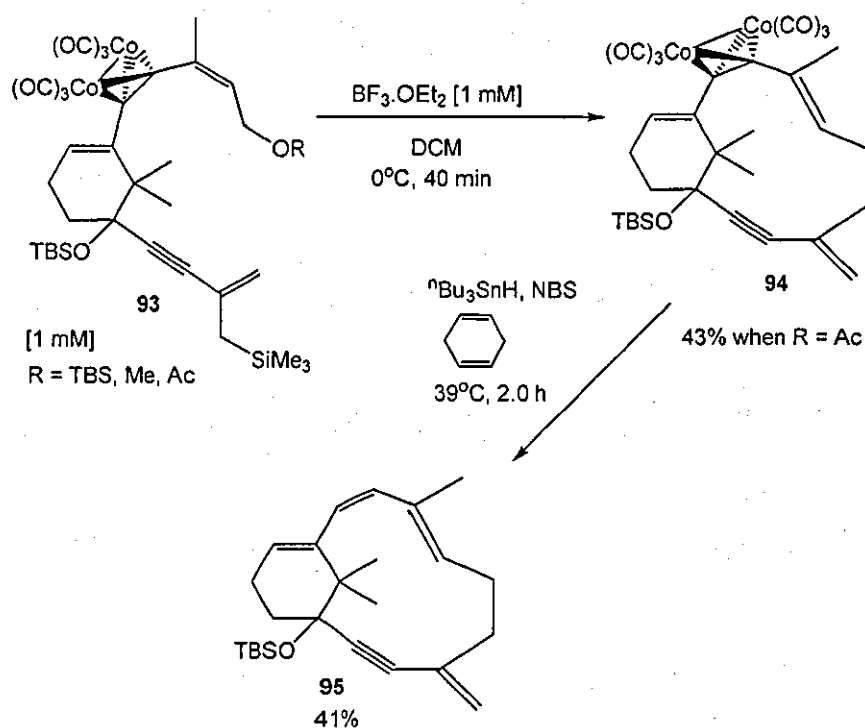


Scheme 28

Investigation into the stereochemical requirements for this reaction has been carried out by McGlinchey et al.<sup>54</sup> by incorporation of the allylalkynylsilane within a rigid terpenoid skeleton, but unfortunately the required transformations failed and dehydration to olefinic products took place, alongside a novel rearrangement to a tricobalt product.

Isobe<sup>55</sup> has used an intramolecular Nicholas reaction between a vinylogous cobalt stabilised carbocation and an allyl silane, in the synthesis of the bicyclo[9.3.1]pentadecane skeleton, common to a series of taxoid diterpenoids (Scheme 29).

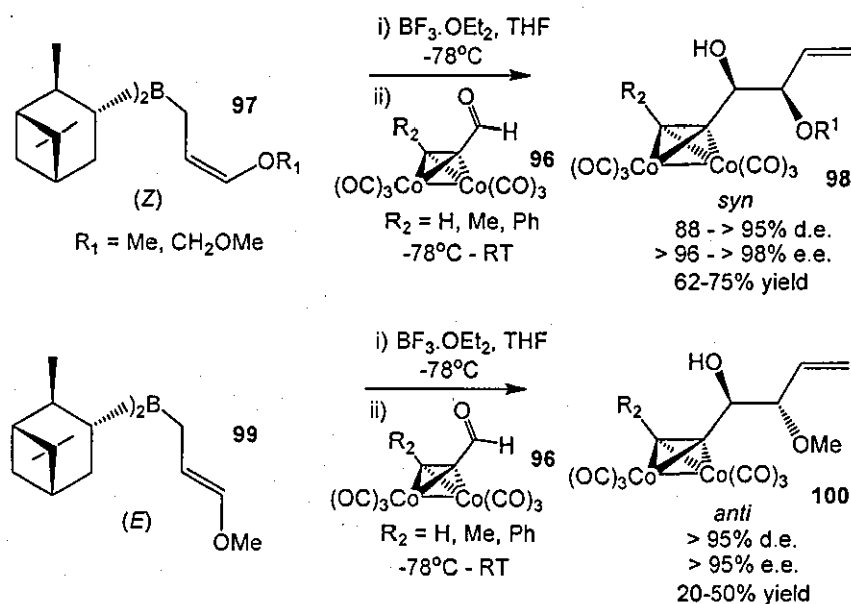
The bicyclic product **95** was obtained on addition of a dilute solution of the cobalt containing complex **93** with a Lewis acid. The reaction proceeded to give a single regioisomer of *trans* stereochemistry, as originally described by Nicholas.<sup>56</sup> During trials with a variety of leaving group and Lewis acid types, it was concluded that the ideal conditions were with an acetate leaving group and boron trifluoride as Lewis acid, resulting in a 43% yield from the acetate.



**Scheme 29**

Nicholas has studied the reaction of cobalt-complexed alkynyl aldehydes **96** with chiral (*Z*)- and (*E*)-( $\gamma$ -alkoxyallyl)diisopinocamphephenylboranes **97** and **99** (Scheme 30). While uncomplexed alkynyl aldehydes reacted under identical conditions to give poor yields (< 15%) and limited enantioselectivity (65-89% e.e.), the corresponding cobalt complexes reacted efficiently with high enantioselectivity and in good yield to fashion (3-alkoxy-4-hydroxy-1-ene-5-yne) $Co_2(CO)_6$  complexes. The (*Z*)-borane **97** created the *syn* product **98**, whilst the (*E*)-borane **99** gave the *anti*-diol derivative **100**.

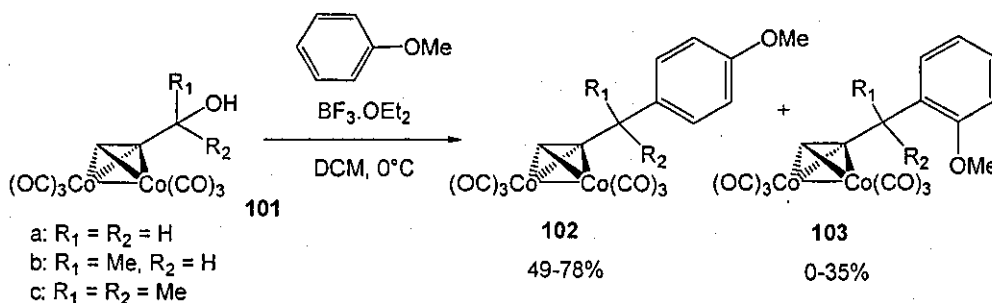




**Scheme 30**

### 1.3.4 Aromatic Nucleophiles

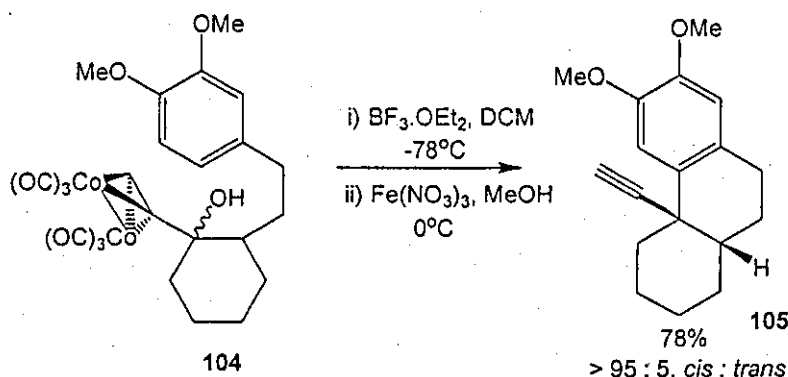
Trapping of aromatic nucleophiles with the  $[(\text{propargylium})\text{Co}_2(\text{CO})_6]^+$  cation was first established by Nicholas et al.<sup>57</sup> in 1977 (**Scheme 31**).



**Scheme 31**

Dissolution of propargylic alcohols **101** in DCM, followed by treatment with anisole and boron trifluoride etherate, produced the aromatic regio-isomers **102** and **103** in good yield. As the steric bulk of the cobalt complex increased, a higher ratio of the least hindered *para*-isomer was formed over the *ortho*-isomer, as expected.

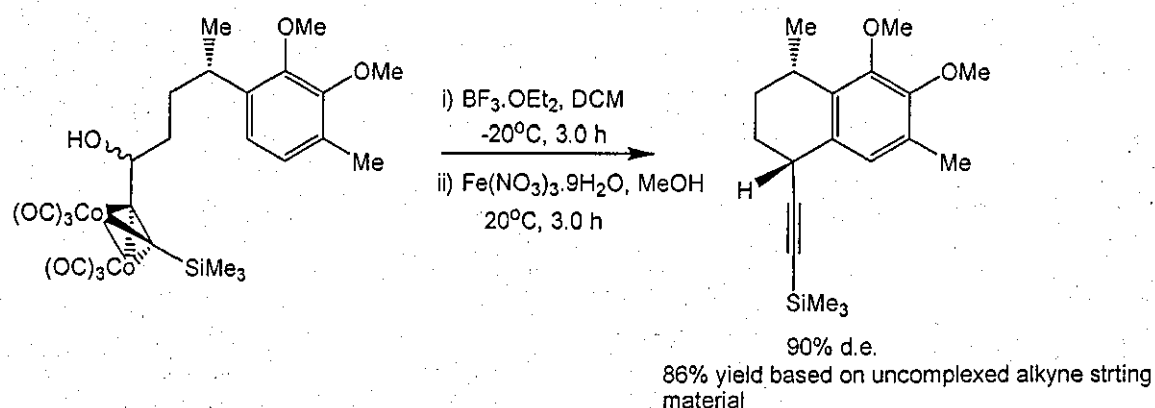
Grove et al.<sup>58</sup> have prepared a *cis*-fused octahydrophenanthrene system, by means of an intramolecular Nicholas reaction. The cobalt complex **104** was treated with boron trifluoride etherate at  $-78^{\circ}\text{C}$ , giving a 78% yield of the tricyclic product **105** after subsequent decomplexation with ferric nitrate at  $0^{\circ}\text{C}$  (Scheme 32).



Scheme 32

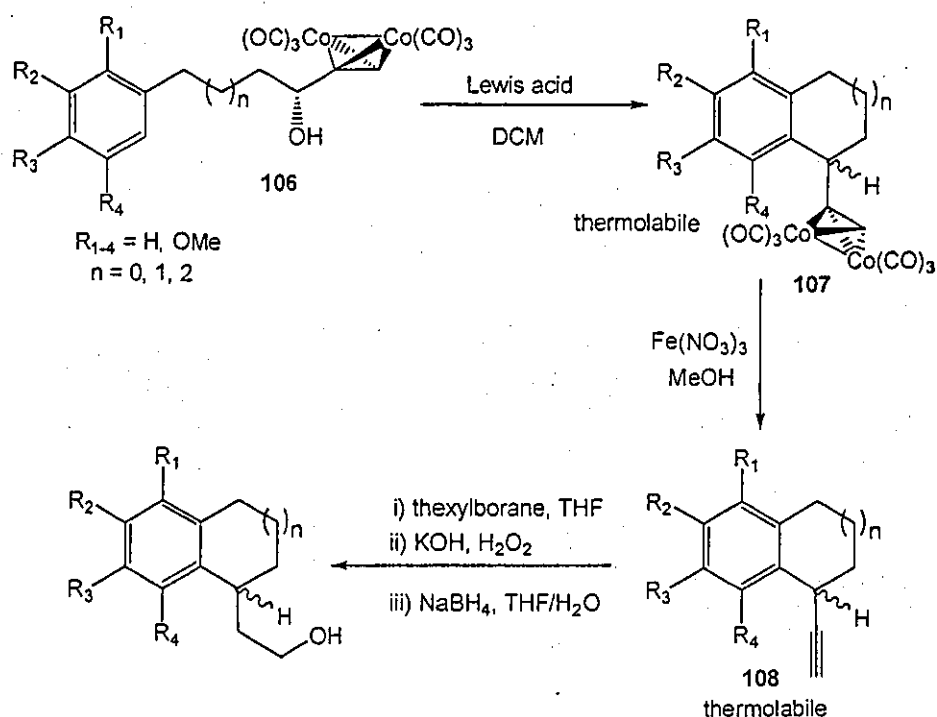
The predominance of the *cis*-isomer is most likely due to the steric interaction between the axial hydrogens of the forming ring and the axial cobalt moiety. In the most stable conformer leading to the *trans*-isomer, three of the axial hydrogens sterically interact with the cobalt group, whereas in the transition state leading to the *cis*-configuration, only one of the axial hydrogens experiences such an interaction. Therefore the less hindered *cis*-isomer should form at a faster rate than the *trans*-isomer, resulting in an increased *cis:trans* ratio.

In their approach to synthesise psuedopterosin G aglycone, Kocienski et al.<sup>59</sup> used an analogous Nicholas based cyclisation. A methyl substituent was situated on the alkyl chain tether, to provide the chiral control therefore negating the necessity for stereoselectivity at the propargylic alcohol centre (Scheme 33).



**Scheme 33**

To determine whether alcohols could cyclise enantiospecifically to give chiral products, Muehldorf et al.<sup>60</sup> studied the reactions with cobalt-complexed optically active secondary propargyl alcohols tethered to electron-rich aromatic rings **106**. It was discovered however, that the intermediate tetrahydronaphthalenes **107** and **108** are thermolabile, consequently a rapid conversion to the final product was necessary before the enantiomeric ratios of the products could be measured (**Scheme 34**). In order to achieve reasonable reaction times, whilst maintaining the stability of the propargylic carbocation configuration, cyclisation was carried out between 0 and  $-65^\circ C$ . The length of the tether, Lewis acid, and the pattern of aromatic substitution were all varied to determine their individual effect upon enantioselectivity.



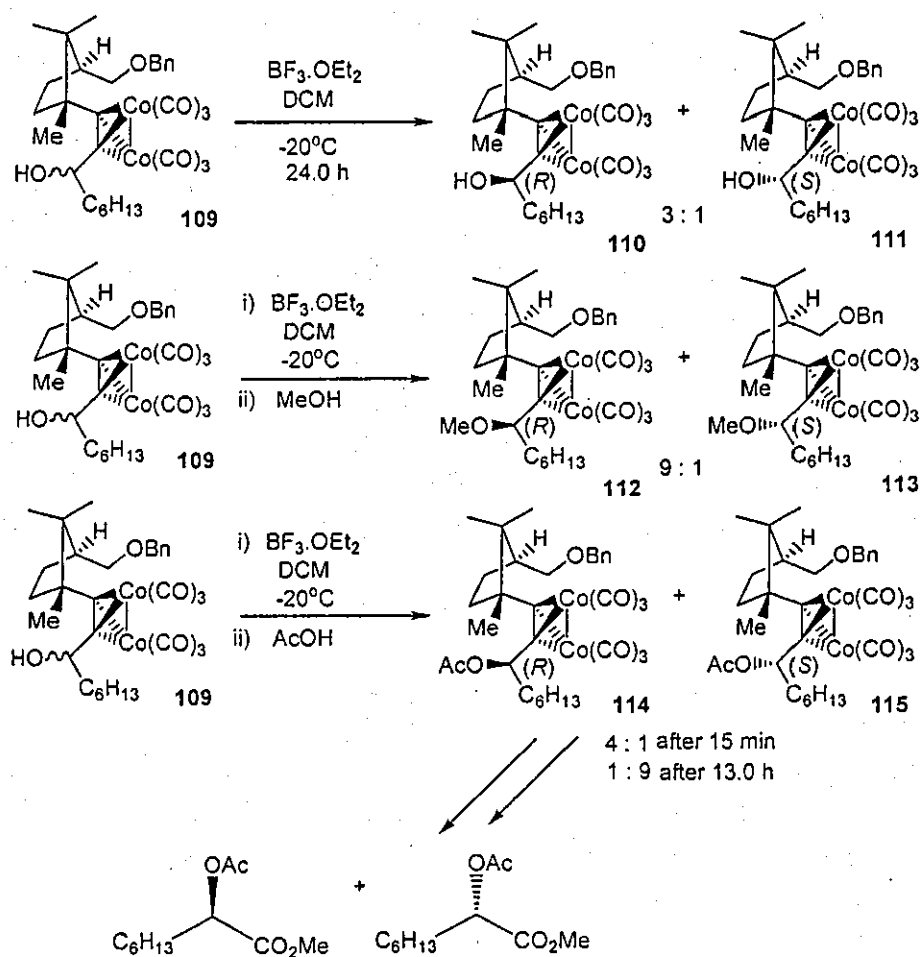
**Scheme 34**

Muehldorf demonstrated that only on the formation of six-membered rings could chirality be transferred, with the best results being achieved when boron trifluoride etherate was used as the Lewis acid. From the pattern of aromatic substitution, there is a requirement to activate the ring towards cyclisation, without sterically hindering the molecule. Yields of 53-73% were achieved, with the highest enantioselectivity of 97% e.e. being achieved with 3,4-dimethoxy substitution at  $-65^\circ\text{C}$ . Reaction with other substitution patterns required slightly higher temperatures, correlating with steric hindrance and their reactivity. The level of enantioselectivity was reduced accordingly, as a result of increased racemisation.

#### 1.4 Reaction with oxygen nucleophiles

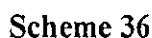
The  $[(\text{propargylium})\text{Co}_2(\text{CO})_6]^+$  cation has become a powerful tool in the synthesis of cyclic ether structures. Due to the number of marine toxins such as maitotoxin,<sup>61</sup> brevetoxins<sup>62</sup> and ciguatoxin<sup>63</sup> containing cyclic ether units, extensive coverage in the literature has been directed towards their synthesis, notably by Isobe,<sup>64-66</sup>

Martín and co-workers<sup>67</sup> have shown that reacting a chiral propargylic cobalt complex **109** with boron trifluoride etherate at  $-20^\circ\text{C}$  for 24.0 h, results in a 3:1 mixture of diastereoisomers **110** and **111** (Scheme 35). In the presence of external oxygen nucleophiles such as methanol or acetic acid, the corresponding methyl ethers **112** or acetates **113** can be obtained with high levels of diastereoselectivity after only 15 min. The addition of a methoxy or acetate group to the product, increases the diastereomeric ratio in comparison to the alcohol product. On reducing the acetate reaction time to 15 min an (*R*) to (*S*) ratio of 4:1 is achieved. However, when the reaction time is extended to 13.0 h, the ratio of diastereoisomers is reversed, so that the (*S*)-isomer predominates by 9:1. Martín, postulates that the increased leaving group ability of the acetate molecule encourages equilibration over the extended period of time and the thermodynamic product is created in excess. The major isomer product can then be purified, decomplexed and reduced to the alkene which is cleaved to give the enantiomerically pure  $\alpha$ -hydroxy acid derivatives **114** and **115**.

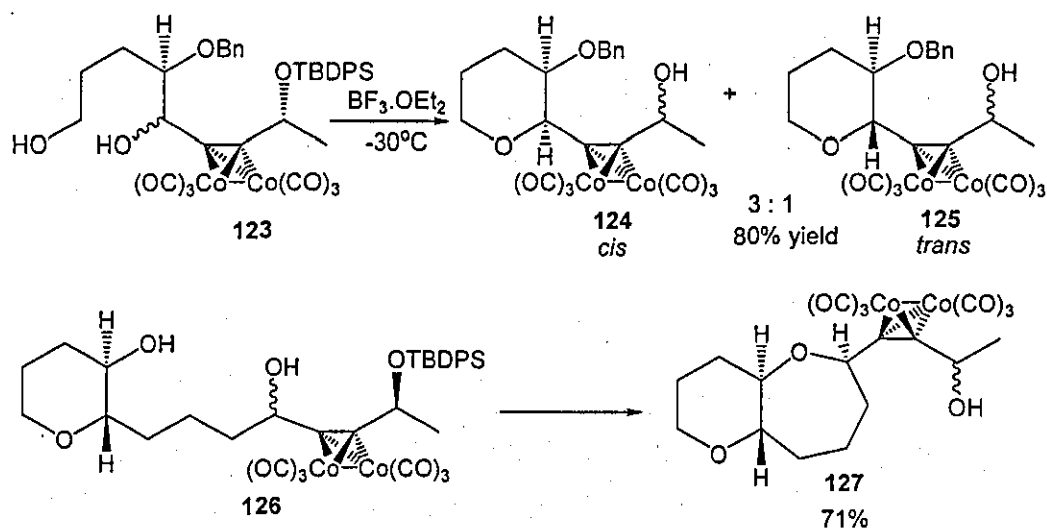


Scheme 35

Martín and Palazón<sup>68</sup> have synthesised medium-sized monocyclic and fused-bicyclic ethers with high stereoselectivity *via* the use of chiral precursors. On reacting linear diols **116** with boron trifluoride etherate, cyclic ethers **117** were obtained in high yield (Scheme 36).



The addition of a second stereocentre at the non-reactive propargylic carbon, however served only to confuse matters. The chiral diol **123** was cyclised to create a 3:1 mixture of *cis*- and *trans*-tetrahydropyrans **124** and **125**, whilst the tetrahydropyran precursor **126** with opposite configuration at the second propargylic centre, cyclised to give a *cis*-fused oxepane **127** exclusively (Scheme 37).

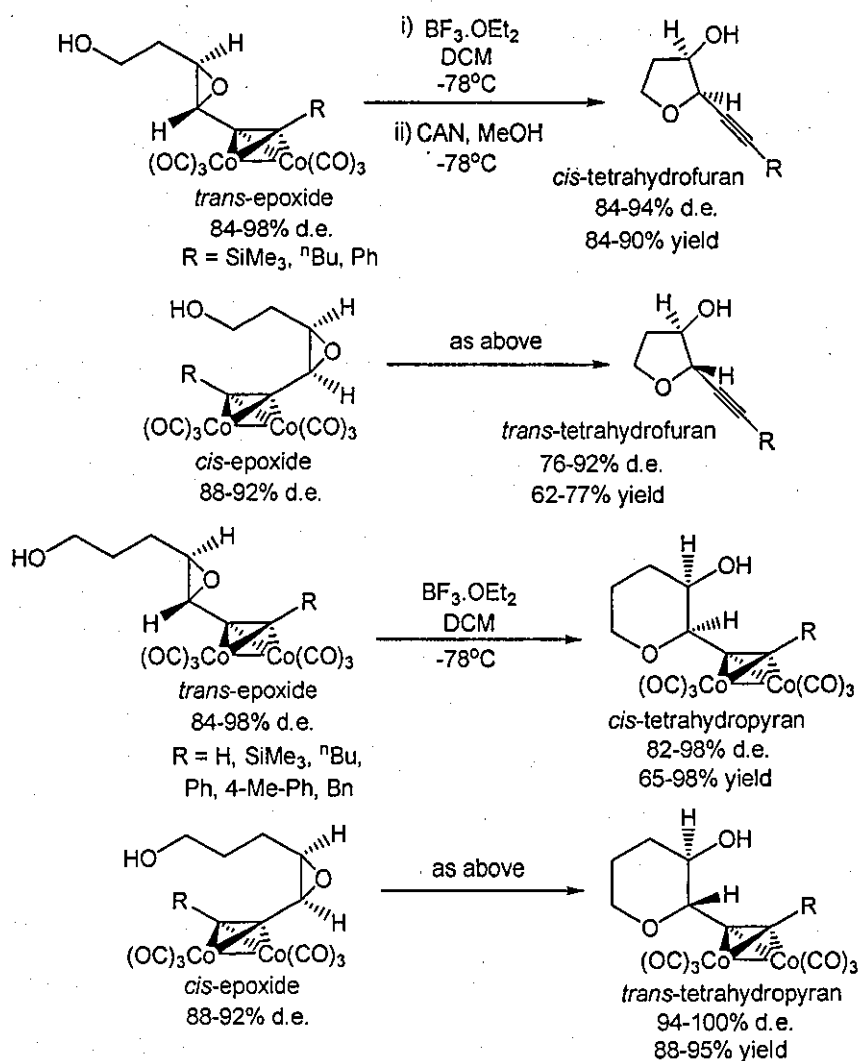


**Scheme 37**

In both of these reactions the silyl protecting groups were lost, along with the chiral information at the secondary propargylic centre, whereas in the previous examples the silyl groups were unaffected (**Scheme 36**). The *O*-silyl protecting groups could be lost due to the enhanced stabilisation of a secondary carbocation, which can be formed from **123** and **126**, over the primary carbocation which is created from removal of the *O*-silyl groups in diols **116** and **121**. From these results it can be concluded that addition of a second chiral centre, although epimerised in the course of the reaction does influence cyclisation.

Mukai and Hanaoka have made a significant contribution in development of novel methods for synthesising cyclic ethers, together with an extensive application to natural product synthesis. On taking cobalt-complexed  $\alpha$ -epoxy-alkynes and catalysing the ring opening by means of treatment with a Lewis acid, Mukai and Hanaoka were able to stereoselectively generate tetrahydrofuran<sup>69</sup> and tetrahydropyran ring systems,<sup>70, 71</sup> by intramolecular trapping with a pendant hydroxyl group (**Scheme 38**).



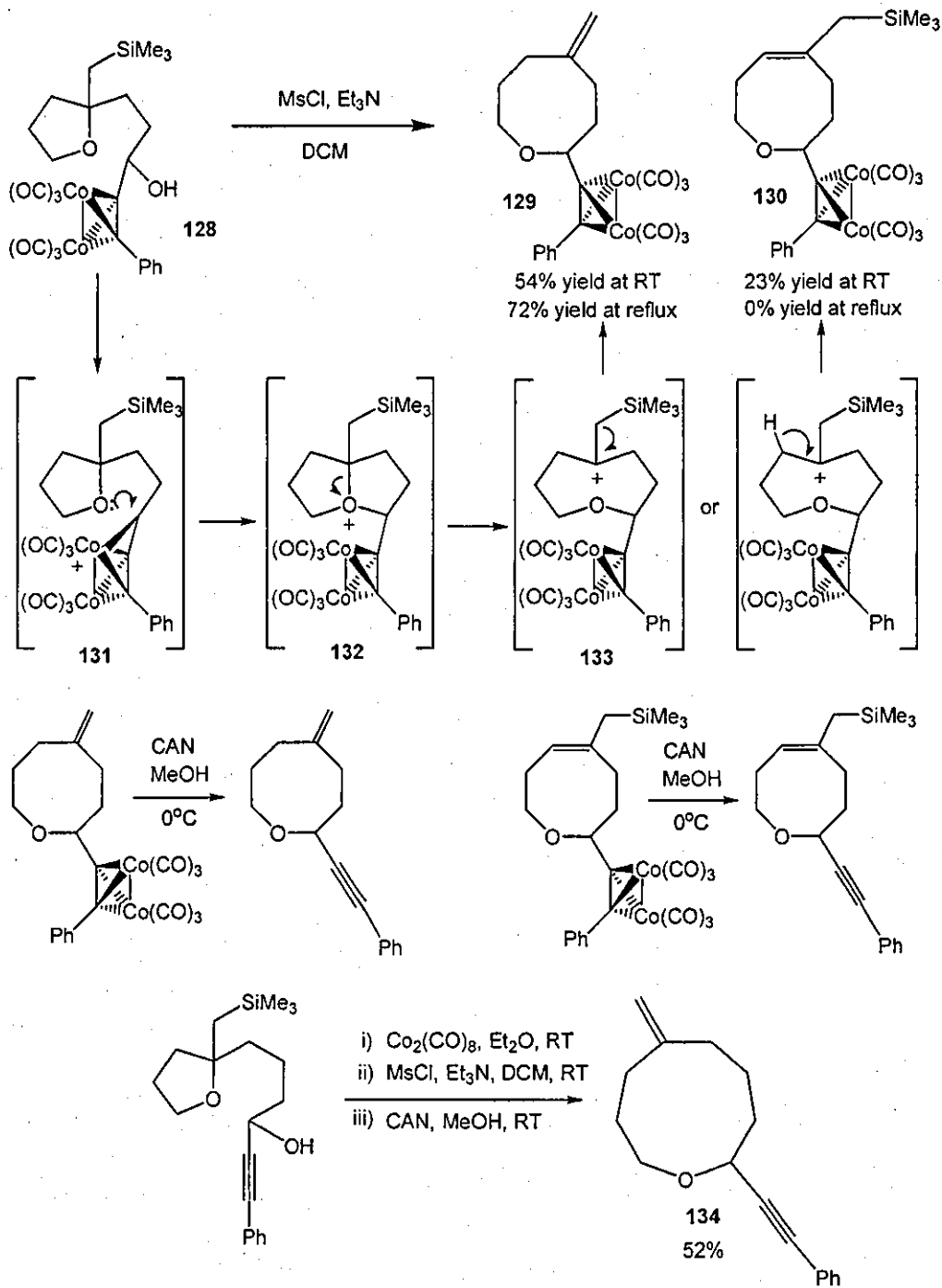


Scheme 38

This *endo*-mode cyclisation is highly stereoselective, presumably occurring *via* a cobalt-assisted double inversion process, with the *cis*-epoxides yielding a *trans* product and *vice versa*. It has also been shown that the nature of the substituent group at the terminal position of the alkyne, has little influence on the outcome of the reaction. The most effective Lewis acids of those studied, proved to be boron trifluoride etherate and TFA.

More recently, Hanoka and Mukai have developed a novel approach to the synthesis of eight and nine membered oxacycles.<sup>10</sup> By treating the cobalt complex **128** with mesyl

chloride and triethylamine in DCM at room temperature, a mixture of oxocanes **129** and **130** was obtained (**Scheme 39**).

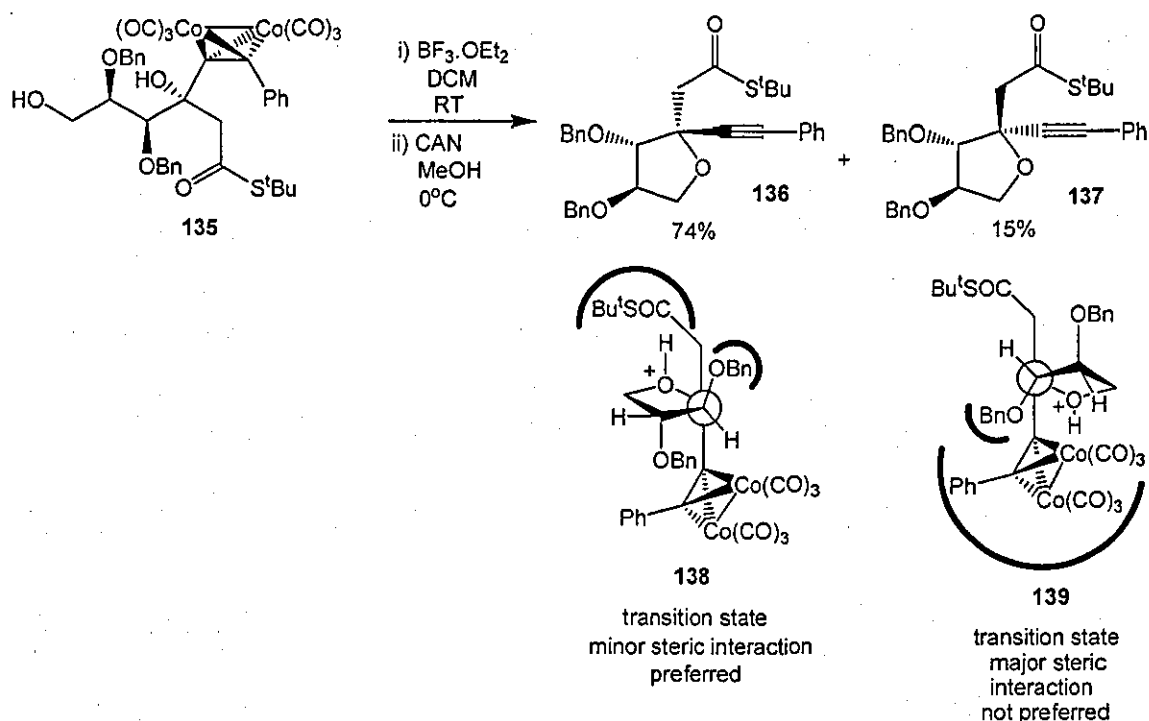


### Scheme 39

Remarkably, the oxygen of the tetrahydrofuran acts as a nucleophile, encouraged by the adjacent trimethylsilylmethyl substituent. Interestingly, when the reaction was carried out under reflux, only the oxocane **127** product from silyl elimination was obtained in 72% yield. After initial loss of the mesylate group to create the [(propargylium)Co<sub>2</sub>(CO)<sub>6</sub>]<sup>+</sup> cation **131**, attack of the tetrahydrofuran oxygen gives the oxonium ion **132**, which can rearrange to the more stable carbocation **133** due presumably to  $\beta$ -stabilisation from the neighbouring trimethylsilyl moiety. Elimination of the trimethylsilyl group and the  $\beta$ -hydride, compete at room temperature to fashion the oxocanes **129** and **130**. The oxonane **134**, was also synthesised using the same methodology. The products could all be decomplexed to the alkynes **129**, **130** and **131** using CAN. Attempts to perform cyclisations using Lewis acids, surprisingly did not yield any oxocane derivatives.

Mukai and Hanaoka<sup>72, 73</sup> have also synthesised (+)-secosyrins **1** and **2**, by means of the stereoselective nucleophilic attack of a hydroxyl group onto a Nicholas cation, to create the highly substituted tetrahydrofurans **136** and **137** (Scheme 40). The alcohol **135** was treated with boron trifluoride etherate, cyclising to give a 5:1 mixture of the tetrahydrofuran diastereoisomers **136** and **137** after CAN demetallation.

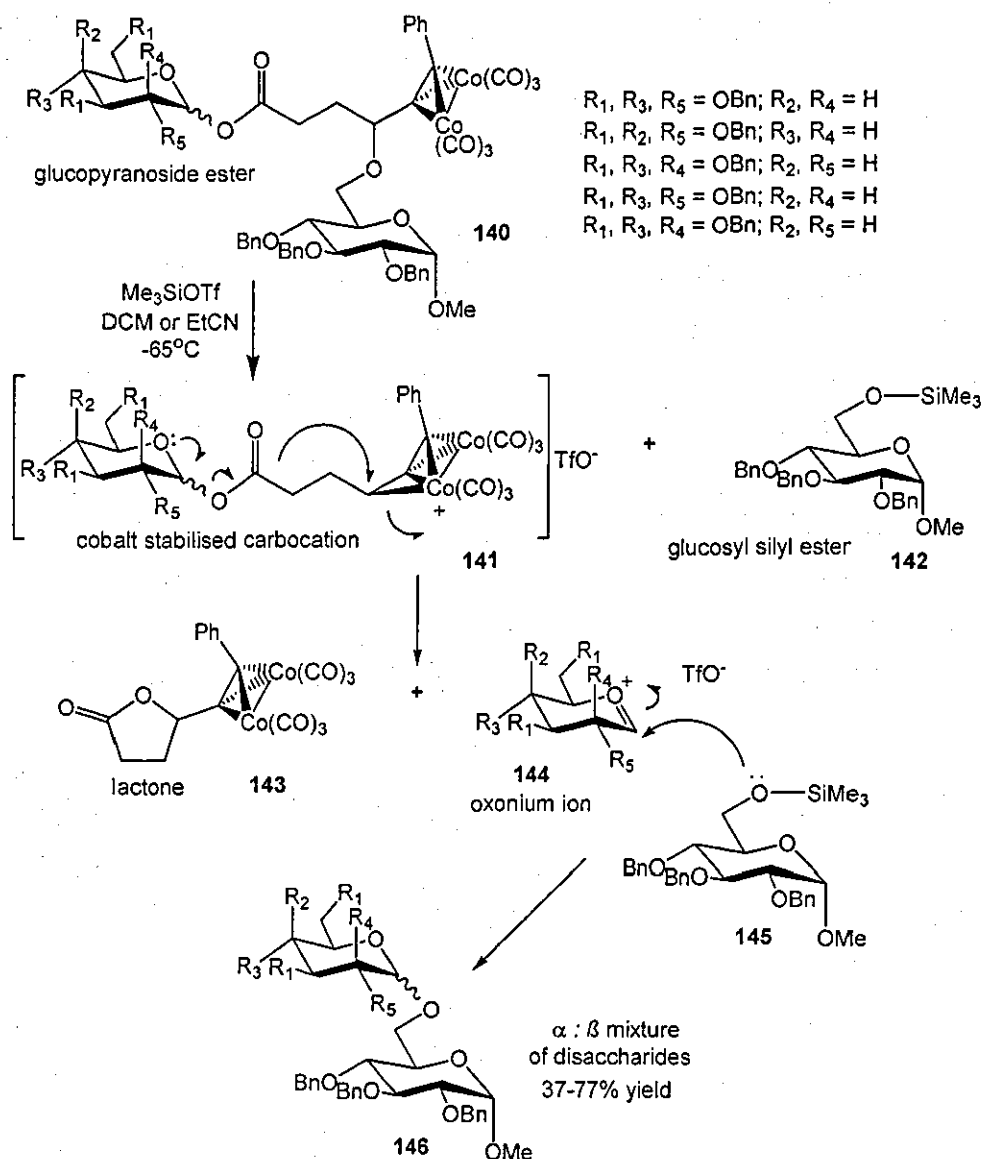
The stereoselectivity can be explained by the steric interactions for the two proposed transition states in the cyclisation reaction. The transition state **138**, which creates the major diastereoisomer **136**, has relatively minor steric interactions between the eclipsed benzyloxy and thioacetate groups. Whereas the transition state **139**, which leads to the undesired product **137**, suffers from a severe interaction between the eclipsed benzyloxy and bulky cobalt complex, therefore accounting for the predominance of **136** over **137**.



**Scheme 40**

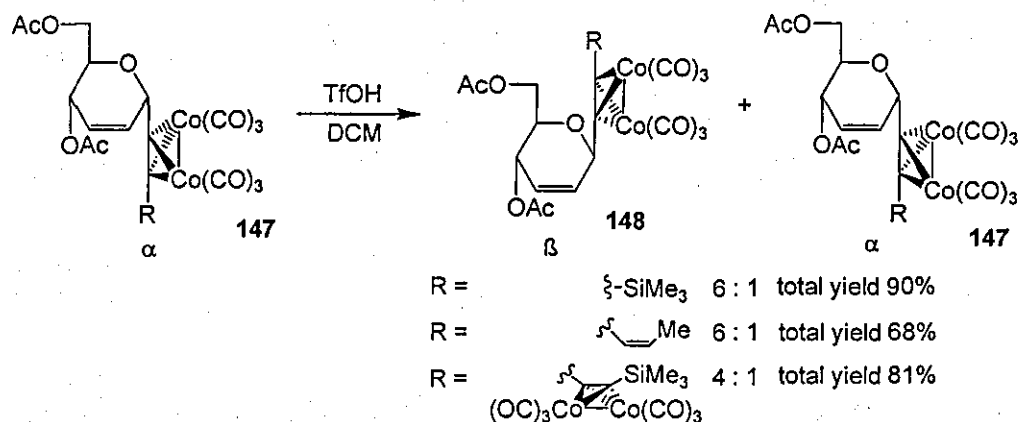
Finally, Mukai and Hanaoka have developed a new glycosylation reaction, utilising the cobalt-complexed 6-phenylhex-5-ynoic acid moiety as a leaving group (**Scheme 41**).<sup>74</sup>

By reacting the glucopyranoside esters **140** with trimethylsilyl triflate at  $-65^\circ\text{C}$ , the glucosyl silyl ether **142** is eliminated and a cobalt stabilised cation **141** is created. The cation then collapses to produce the lactone **143** and oxonium ion **144**, which is rapidly captured by the glucosyl silyl ether **145** to give a mixture of  $\alpha/\beta$ -disaccharides **146**. The ratio of  $\alpha/\beta$ -isomers is dependent on the solvent, stereochemistry of the  $\text{R}_4$  and  $\text{R}_5$  substituents and whether *O*-benzyl ether or *O*-benzoyl ester protecting groups were used.



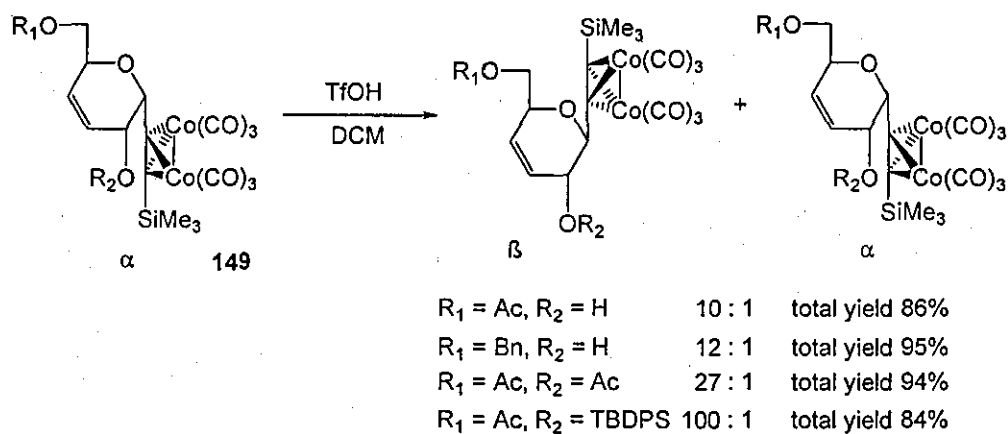
**Scheme 41**

Isobe is another major contributor in the application of [(propargylum)Co<sub>2</sub>(CO)<sub>6</sub>]<sup>+</sup> cations to capture oxygen nucleophiles. On discovery of epimerisation at the C-1 position of pyranose rings by reacting complexed alkynyl substituents with trifluoromethanesulfonic acid, the alkynyl substituent can transform from the  $\alpha$ - to  $\beta$ -position in good yield (**Scheme 42**).<sup>75, 76</sup> The  $\alpha$ -substituted- $\Delta^{2,3}$ -pyranose derivatives **147**, were epimerised to a  $\geq 4:1$  ratio of  $\beta$ : $\alpha$ -isomers **148** and **147** in good yield.



**Scheme 42**

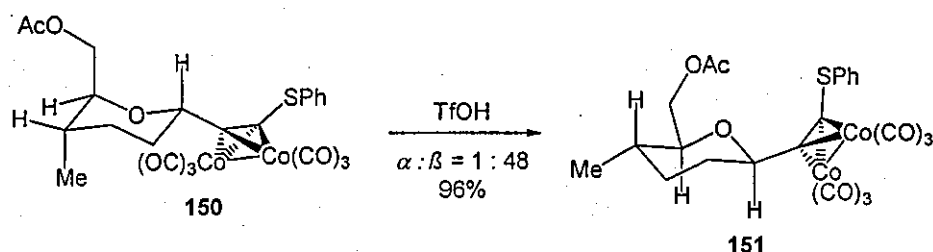
Isobe states that the preferential formation of the  $\beta$ -isomer, is due to the minimisation of 1,2-diaxial steric interactions in the lowest energy boat-form conformation of the pyranose structures. The larger the steric interactions present, the greater is the energy difference between the two isomers. Therefore, increasing the number and size of substituent groups on the ring, should create a superior  $\beta$ - to  $\alpha$ -isomer ratio, which is evident when  $R_2$ =TBDMS as a ratio of 100:1 is achieved from 149 (Scheme 43).



**Scheme 43**

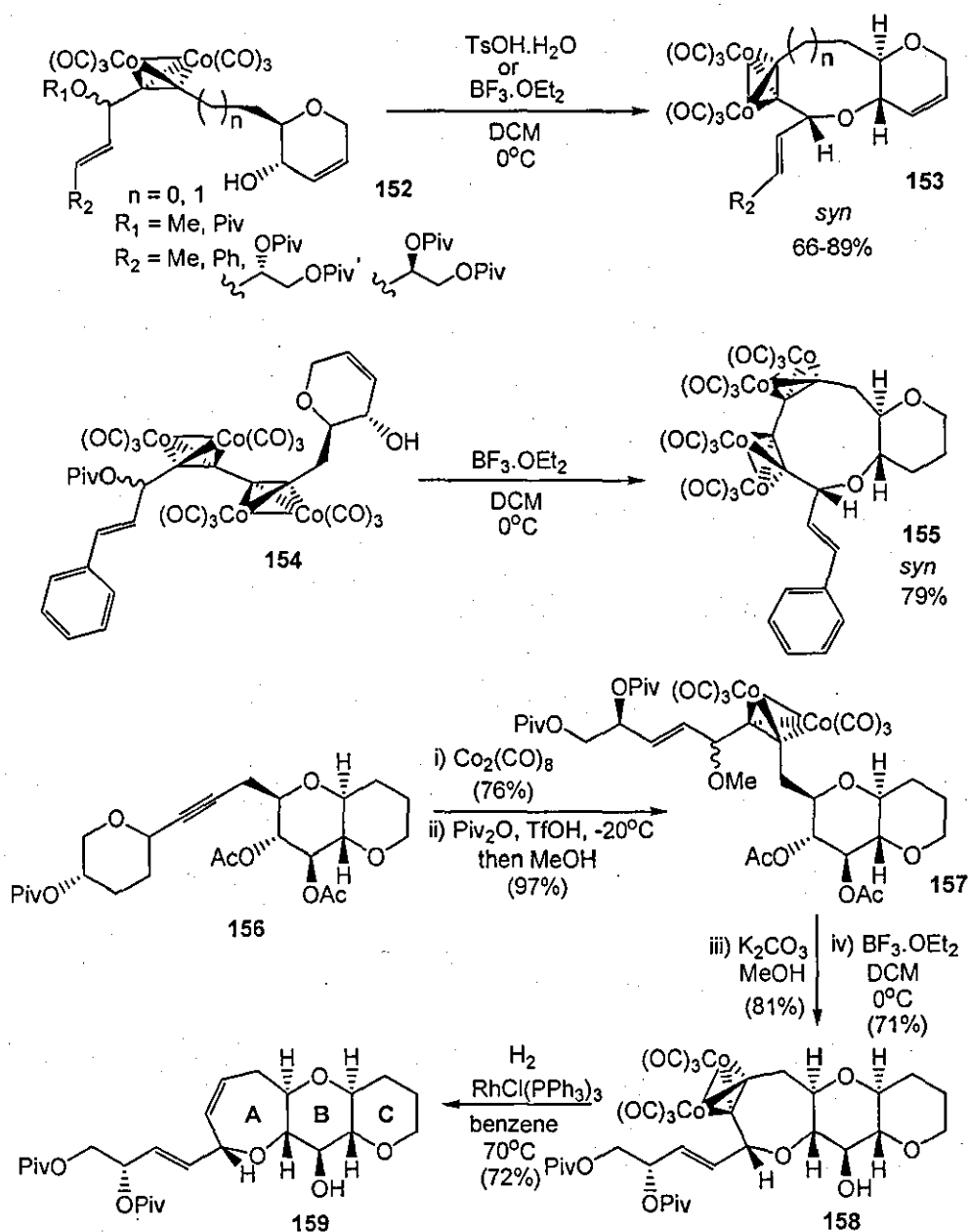
Isobe, then applied this epimerisation strategy to the phenylthioalkynylpyranoses 150, in studies towards segment C, and in the complete synthesis of the natural product

tautomycin.<sup>77, 78</sup> The epimerisation of pyranose **150**, successfully created a 48:1 ratio of  $\beta$ : $\alpha$ -isomers **151** and **150** in 96% yield, most likely due to both the methyl and acetoxymethyl groups preferring to adopt equatorial positions (Scheme 44).



**Scheme 44**

Combining all of the ring closing and opening methodology, Isobe<sup>79</sup> directed studies toward the synthesis of fused [5.4.0], [6.4.0] and [7.4.0] bicyclic ethers similar to those produced by Martín and Palazón. Culmination of this work has led to the creation of many of the ring structure segments of ciguatoxin, including the left-hand A/B/C (Scheme 45)<sup>80-82</sup> and E/F/G/H rings,<sup>83</sup> together with the right hand H/I/J ring systems.<sup>85</sup> By reacting *trans*-alkenes **152**, carrying a six membered ring alcohol on a cobalt-protected alkyne tether with boron trifluoride etherate, [5.4.0] and [6.4.0] ring systems **153** were formed with the *syn* stereoisomer predominating. To synthesise the desired ring system **155**, a tether containing two cobalt-protected alkynes **154** was required. In the synthesis of the A/B/C rings of ciguatoxin, a  $\Delta^{2,3}$ -pyranose substituted with an alkyne-tethered [4.4.0] bicyclic ether **156** was complexed with  $\text{Co}_2(\text{CO})_8$ , before ring opening to give the *trans*-alkene **157**. Alkene **157** was subsequently cyclised with treatment of boron trifluoride etherate to the tricycle **158**, before reductive decomplexation over Wilkinson's catalyst to yield the required compound **159** (Scheme 45).



Scheme 45

Isobe et al.<sup>85</sup> published in 1998 a review of their research into the use of the Nicholas reaction, in particular describing in more detail its use in the synthesis of sugar acetylenes and their derivatives.

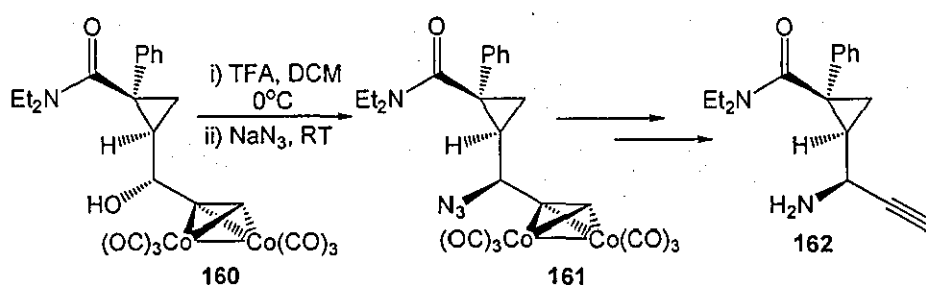


## 1.5 Reaction with other heteroatom nucleophiles

There is limited reported chemistry in the literature involving nucleophilic reactions between non-oxygen heteroatoms and cobalt-stabilised propargylic cations. However there are a few reactions of interest in the scope of the Nicholas reaction.

### 1.5.1 Azide Nucleophiles

Shuto et al.<sup>86</sup> successively treated the propargylic alcohol **160** with trifluoroacetic acid and sodium azide, creating the azide **161** as the exclusive product. Transformation of the azide product into an NMDA receptor antagonist **162** then took place (Scheme 46).

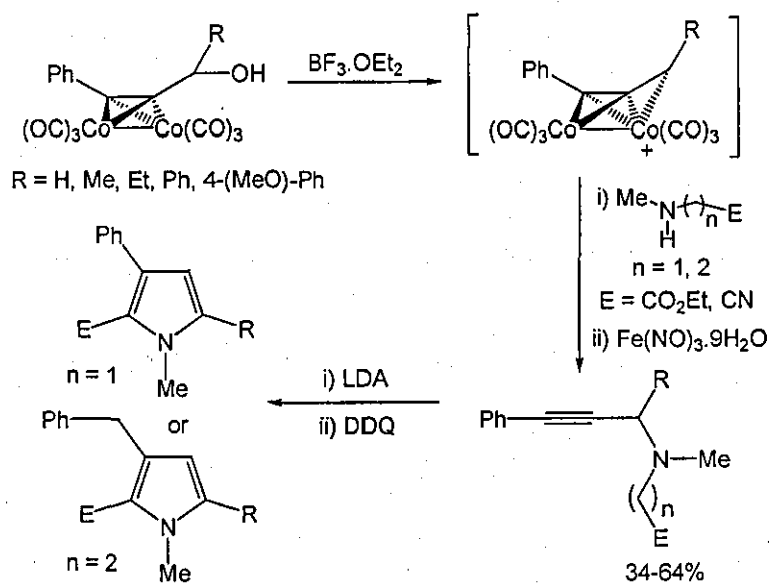


Scheme 46

Shuto postulates that the propargylic cation is not only stabilised by the cobalt-moiety, but also the  $\alpha$ -cyclopropyl group. The stereochemistry is thought to be due to steric interactions, therefore nucleophilic attack is directed from the least-hindered face of the preferred (*S*)-*trans* conformation of the carbocation.

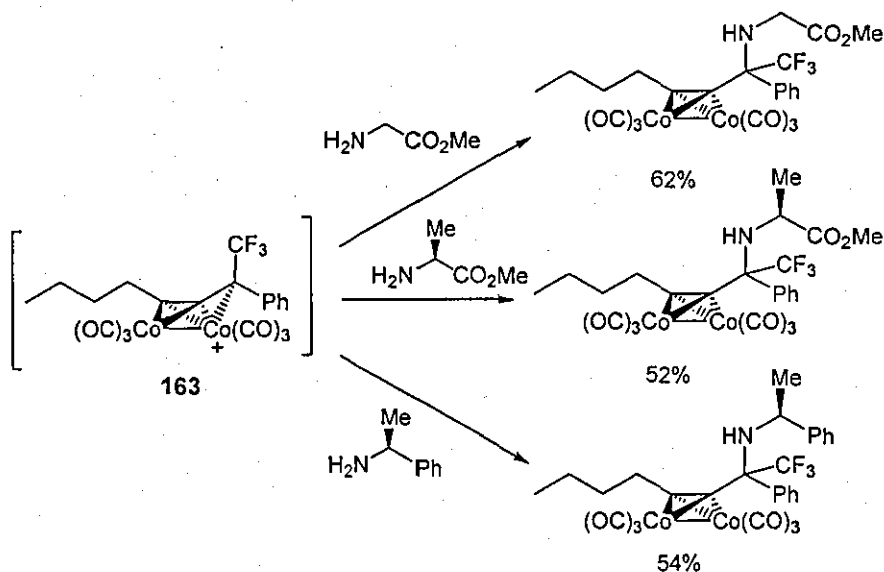
### 1.5.2 Amine Nucleophiles

Yeh et al.<sup>87</sup> have reacted the [(propargylum)Co<sub>2</sub>(CO)<sub>6</sub>]<sup>+</sup> cation with  $\alpha$ - and  $\beta$ -amino acid derivatives, to give propargylamines in good yield, which were later cyclised to furnish pyrroles (Scheme 47).



Scheme 47

Primary amines have been investigated by Bonnet-Delpon et al.<sup>88</sup> After generation of  $\alpha$ -trifluoromethylcarbocations **163**, reaction with simple amino acid esters and optically active  $\alpha$ -methylbenzylamine was performed in good yield (Scheme 48).

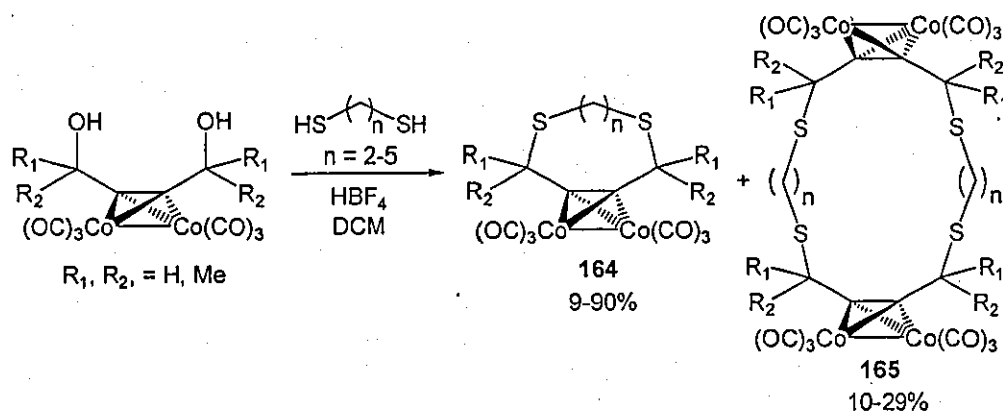


Scheme 48

This is the first reported synthesis and reaction of a cobalt-stabilised  $\alpha$ -trifluoromethyl-propargylium cation. This demonstrates a possible route for the production of compounds containing a  $\text{CF}_3$ -substituted quaternary carbon.

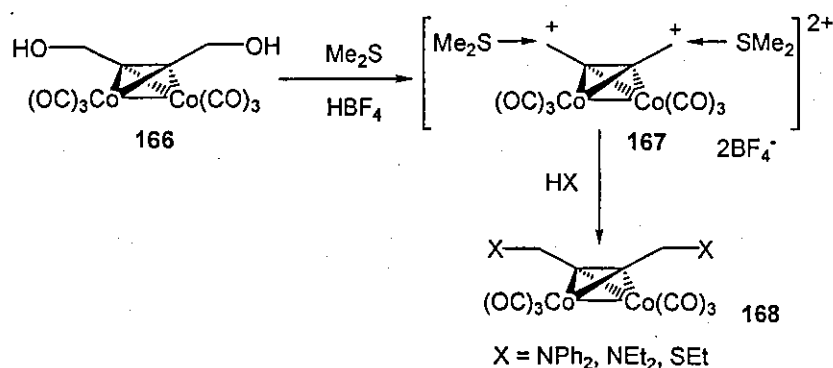
### 1.5.3 Sulfur Nucleophiles

The only research group that have reported significant sulfur chemistry utilising the Nicholas propargylium carbocation (beyond the use of thiophenol as a nucleophilic trap for the cobalt-stabilised cations) is Went et al.<sup>89</sup> Simple complexed diols were reacted with alkyl dithiols in the presence of tetrafluoroboric acid (Scheme 49), and the desired cyclic dithia-alkyne complexes **164** could be isolated in a varied 9-90% yield, with the dimeric compound **165** also being created in poor yield (10-29%).



Scheme 49

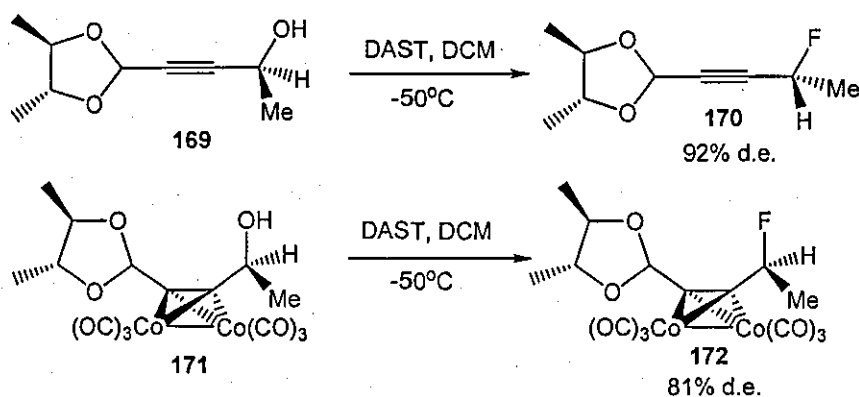
Earlier work by Went et al.<sup>90</sup> described the synthesis of an air stable form of the  $[(\text{propargylium})\text{Co}_2(\text{CO})_6]^+$  cation **167**, obtained by protonation of a diol complex **166** and trapping with dimethylsulfide in high yield. The air stable orange solid dication can be stored in air for up to a year without decomposition, whilst still being reactive with respect to nucleophiles, giving the expected products **168** on treatment with secondary amines and thiols (Scheme 50).



Scheme 50

#### 1.5.4 Fluoride Nucleophiles

Grée et al.<sup>91</sup> were first to report the use of fluoride as the capturing nucleophile in the Nicholas reaction. By treating the chiral propargyl alcohols **169** with DAST at  $-50^\circ\text{C}$ , the corresponding fluoride products **170** were created with an inversion of stereochemistry. When the corresponding chiral cobalt-protected propargyl alcohol **171** was reacted under identical conditions, the predicted fluoride product **172** was formed, but with retention of stereochemistry (Scheme 51).



Scheme 51

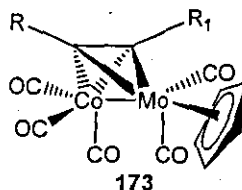
The diastereoselectivity of the products on reaction of **171** with DAST was dependent on the temperature used, which is consistent with the recognized isomerisation of

$[(\text{propargylium})\text{Co}_2(\text{CO})_6]^+$  cations.<sup>24</sup> Upon reaction at  $-80^\circ\text{C}$ , a d.e. of 86% was achieved, whereas at  $20^\circ\text{C}$  it was reduced to only 40%. At lower temperatures isomerisation is slow, compared to the relative rate of nucleophilic attack from the fluoride anion, so the retention of stereochemistry is maintained. As the temperature rises, the rate of isomerisation increases and the stereoselectivity is reduced.

Fluoride ions have previously been shown to trap tertiary carbocation intermediates, formed on reaction between cobalt-stabilised cations and alkenes.<sup>34, 92-93</sup>

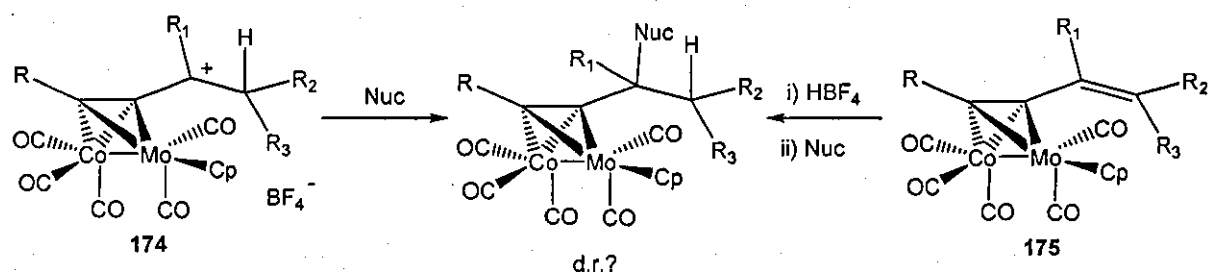
## 1.6 Extension of Nicholas methodology

Diastereoselectivity has been achieved using homobimetallic alkyne systems,<sup>21, 23, 26</sup> both by transfer of chiral information already in the molecule and taking advantage of sterically favourable transition states. Homobimetallic complexes are not chiral, as the two metal centres are stereospecifically equivalent; therefore approach of a nucleophile is equally probable from either face of the molecule. Adoption of a desymmetrised metal core should encourage chiral control from a removable auxiliary, as the two faces are now sterically differentiated, but only limited research has been carried out utilising this methodology.<sup>94-</sup>  
<sup>96</sup> We proposed the use of a heterobimetallic system such as cobalt-molybdenum alkyne complexes **173**, whereby the possibility of diastereo- and enantioselectivity can be achieved in the products formed. Enantioselective reactions using a single enantiomer of a heterobimetallic complex can be achieved, as the metal core is inherently chiral with desymmetrisation of the complex occurring when unsymmetrical alkynes are employed (Scheme 52).



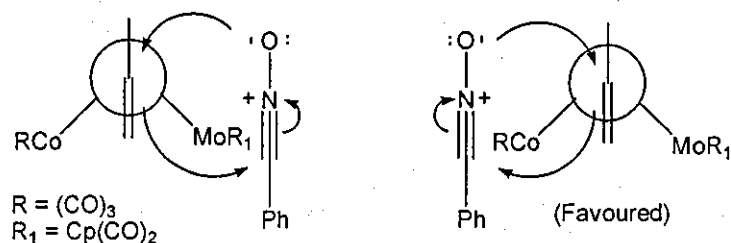
**Scheme 52**

Initially, we intend to synthesise propargylic Nicholas salt **174** and enyne **175** complexes and explore the diastereoselective capability the heterobimetallic core creates during nucleophilic attack to these salt and enyne complexes (Scheme 53). This primary research can be extended to both, intramolecular addition to form ring systems and chiral substrates to obtain enantioselectivity.



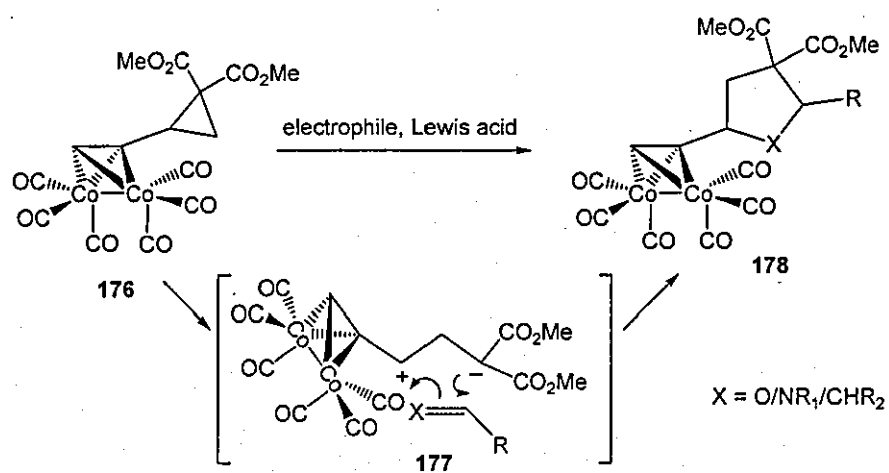
**Scheme 53**

We are also interested in developing new methodologies utilising bimetallic alkyne complexes. Nicholas<sup>97</sup> has reported 1,3-dipolar cycloaddition between homobimetallic enynes and benzonitrile oxide. We wanted to extend this cycloaddition to heterobimetallic enynes, thus establishing diastereoselectivity, with a preference of dipolar attack *via* the cobalt face of the molecule (**Scheme 54**).



**Scheme 54**

Another area of interest is a potentially novel cyclisation of a 1,3-dipole with electrophiles. Ring opening of a homobimetallic diester cyclopropane **176**, should create a dipole with a positive charge stabilised at the propargylic position and the diester stabilising a negative charge **177**. Hopefully, the dipole will then react with electrophiles to obtain ring systems **178** (**Scheme 55**). Subsequent development of heterobimetallic systems should then enable increased diastereoselectivity.



**Scheme 55**



## **2.0 Results and Discussion**

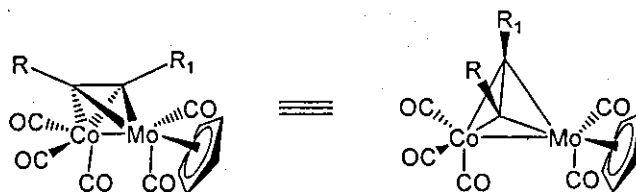
### **2.1 Heterobimetallic alkyne systems**

#### **2.1.1 Background**

The application of homobimetallic alkyne systems in the Nicholas reaction has been extensively explored and reported in the literature.<sup>98</sup> Although diastereoselectivity has been achieved in specific cases,<sup>21, 23, 26</sup> there has been very little research on desymmetrised systems encouraging chiral control from a removable auxiliary.<sup>94-96</sup> Therefore, upon the use of a heterobimetallic system such as cobalt-molybdenum alkyne complexes, it may be possible to induce diastereo- and enantioselectivity in the products formed, and this was our first research area.

#### **2.1.2 Enantiospecific rationale for the heterobimetallic core**

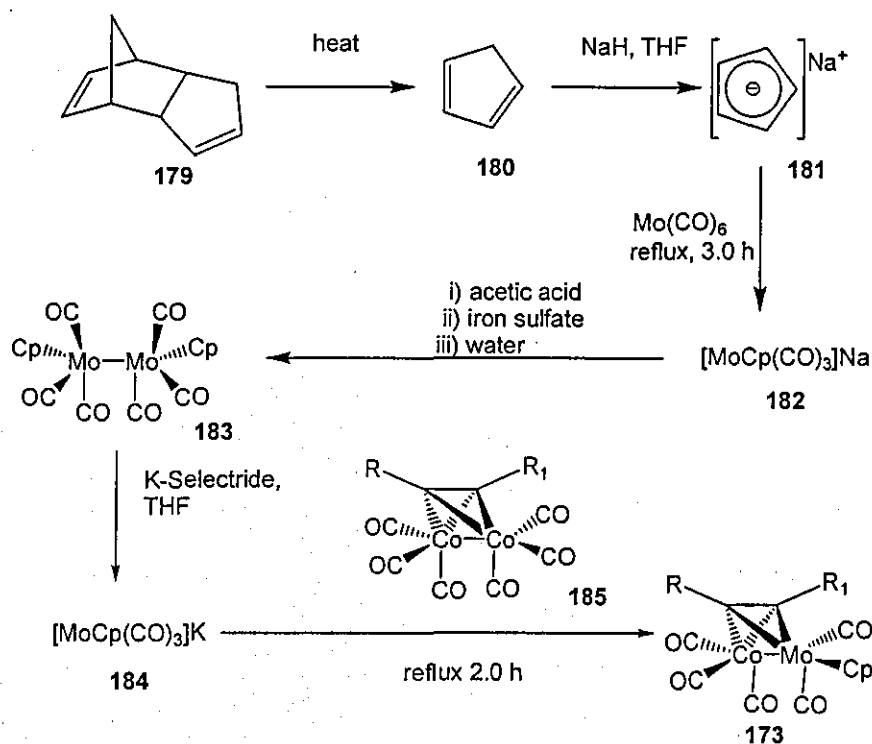
Enantioselective reactions using heterobimetallic complexes can be achieved, as the metal core is inherently chiral with desymmetrisation of the complex occurring when unsymmetrical alkynes are employed. Homobimetallic complexes are not chiral, as the two metal centres are equivalent. X-Ray crystallographic data of Co-Mo heterobimetallic complexes show the  $C_2Co/Mo$  metal core as an exploded tetrahedron with the metal-metal bond perpendicular to the alkyne carbon-carbon bond, as in the dicobalt hexacarbonyl system. The alkyne substituents R and R<sub>1</sub> are no longer in a linear arrangement (**Scheme 56**).



(Scheme 56 – the general heterobimetallic complex as an exploded tetrahedron)

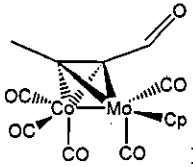
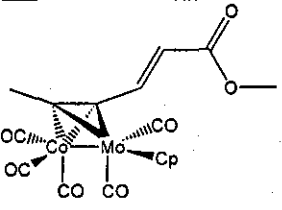
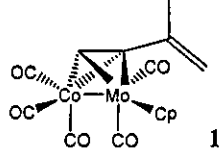
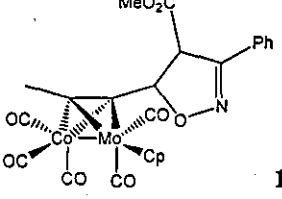
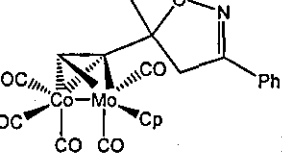
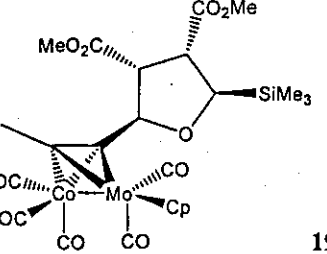
### 2.1.3 Synthesis of the heterobimetallic core

The formation of heterobimetallic complexes was carried out as a series of reactions (Scheme 57). Initially dicyclopentadiene **179** was cracked at 175°C, distilling off the cyclopentadiene **180** fraction boiling between 35-45°C. This was deprotonated to create the cyclopentadienyl anion **181** using NaH in THF at 0°C, before refluxing for 3.0 h with molybdenum hexacarbonyl to yield the cyclopentadienyl molybdenum tricarbonyl anion **182**. Upon further treatment with a filtered solution of acetic acid, iron sulfate and water the air stable molybdenum cyclopentadienyl tricarbonyl dimer **183** was precipitated as a purple crystalline powder. The molybdenum cyclopentadienyl tricarbonyl dimer could then be taken at whatever time, or quantity required for isolobal displacement in a dicobalt hexacarbonyl alkynyl complex. To create the heterobimetallic equivalent **173**, the nucleophilic cyclopentadienyl molybdenum tricarbonyl anion **184** must be created by reductive cleavage of the molybdenum-molybdenum bond on treatment with either lithium, potassium or sodium tri-*sec*-butyl borohydride (L-, K- or N-Selectride), with an almost immediate loss of hydrogen. The dicobalt hexacarbonyl complex **185** can then be added and heated to reflux in THF. Reductive cleavage of metal carbonyl dimers using trialkylborohydrides was first reported by Gladysz,<sup>99</sup> when investigating the preparation of metal alkyl and metal acyl complexes.



(Scheme 57 - stepwise synthesis for isolobal displacements)

Isolobal displacement of a cobalt tricarbonyl species by cyclopentadienyl molybdenum dicarbonyl took place in variable yields, 25-83% with a variety of dicobalt hexacarbonyl complexes upon refluxing in THF for up to 1.5 h, after initial formation of the cyclopentadienyl molybdenum tricarbonyl anion with L-Selectride (Table 1). On investigation with K-Selectride yields were improved to a moderate to excellent 40-90% after refluxing for 2.0 h. K-Selectride also had the added advantage of cleaner reactions and purification with column chromatography. One attempt at displacement on the dicobalt hexacarbonyl-butynal complex using N-Selectride showed similar characteristics to L-Selectride, comparing time scale, yield and work up, therefore no further investigation was undertaken with this reagent.

Displaced product	Borohydride	Yield (%)	d.r.	s/m (%)
 186	L-Selectride K-Selectride N-Selectride	83 90 72	n/a	0 3 0
 187	L-Selectride K-Selectride	69 75	n/a	0 0
 188	L-Selectride K-Selectride	60 70	n/a	0 0
 189	L-Selectride K-Selectride	25 40	1 : 1 1 : 1	0 0
 190	L-Selectride K-Selectride	25 40	1 : 1 1 : 1	0 0
 191	K-Selectride	51	1.3 : 1	0

(Table 1 – isolobal displacement of dicobalt hexacarbonyl complexes)

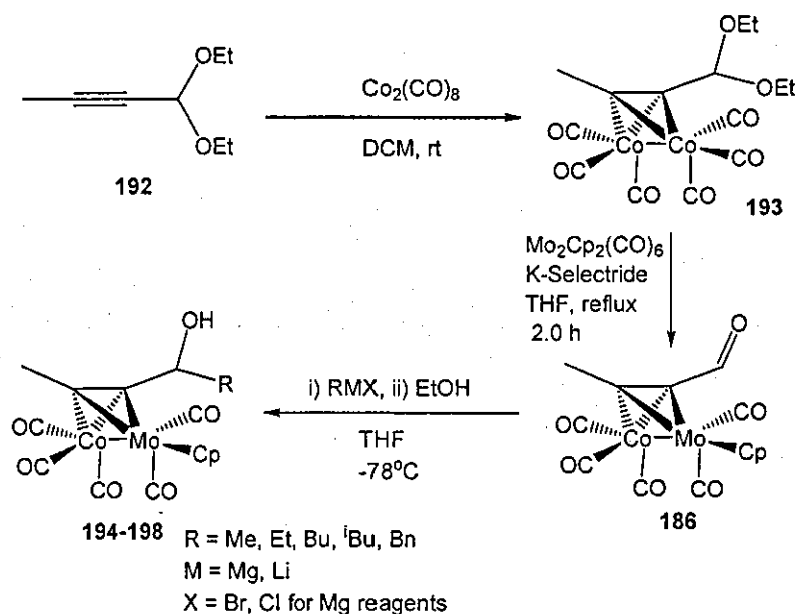
In the isolobal displacement of dicobalt isoxazoline complexes 189 and 190 with L- and K-Selectride, lower than expected yields were achieved. It is not clear where the complex is lost as only the coloured fractions were isolated by column chromatographic purification.

The nitrogen-oxygen bond may be cleaved under the applied conditions, therefore promoting higher levels of decomposition. Further research is needed to confirm this assumption. A higher yield of 51% was achieved with the highly substituted furan derivative **191**, with a small diastereoselective preference of 1.3:1. Increased yields of 70, 75 and 90% for enyne and aldehyde complexes **187**, **188** and **186** were achieved, suggesting that more stable substrates are increasingly tolerant to the displacement conditions and consequently give higher yields.

## 2.2 Exploration of heterobimetallic Nicholas salt complexes

### 2.2.1 Grignard addition to heterobimetallic-butyne

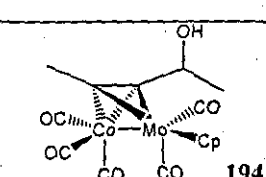
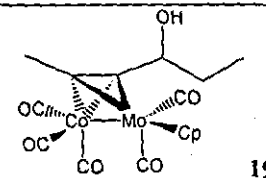
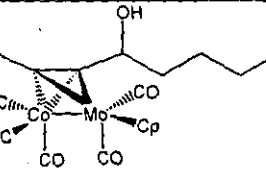
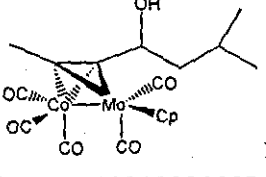
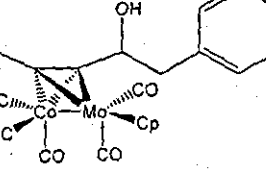
Initially 2-butyne diethyl acetal **192** was complexed with dicobalt octacarbonyl to create dicobalt hexacarbonyl-2-butyne diethyl acetal **193**. This was isolated and subjected to an *in situ* isolobal displacement-deprotection reaction when added to the pre-formed molybdenum cyclopentadienyl tricarbonyl anion **184**. Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-butyne **186** was furnished in a 90% overall yield for the two steps, after a 2.0 h reflux in THF. Grignard additions to the heterobimetallic aldehyde at  $-78^{\circ}\text{C}$  in dry THF, generated the corresponding alkyl alcohol complexes **194-198** in excellent yield (93-96%) and in reasonable to very good d.r. (6:1-10:1), after stirring at  $-78^{\circ}\text{C}$  for 2.0 h (Scheme 58, Table 2).



(Scheme 58 - synthesis of propargylic alcohol complexes)

The methods, yields and diastereoselectivity were in agreement with the results previously reported by our group.<sup>100</sup> In general, as the steric requirements increased so did the level of stereocontrol. For example, the bulky *i*-BuMgCl derivative provided a 10:1 d.r. upon

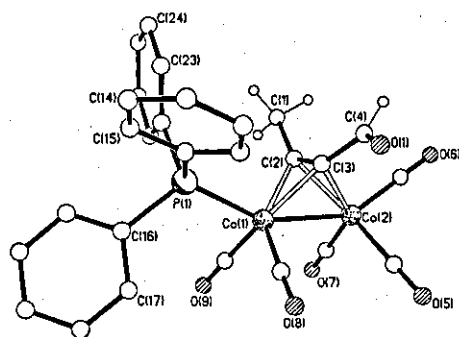
addition to the heterobimetallic aldehyde **186**, in contrast this reduced to a 6:1 d.r. with the least sterically encumbered MeMgBr nucleophile. These results provide evidence for the diastereoselective power of the heterobimetallic cobalt-molybdenum centre, with larger nucleophiles showing a greater preference on approaching the aldehyde from the cobalt face of the molecule, by analogy with the following results.

Nucleophile product	Nucleophile	Yield (%)	d.r.
 <b>194</b>	MeMgBr	95	6 : 1
 <b>195</b>	EtMgCl	96	10 : 1
 <b>196</b>	<i>n</i> -BuLi	93	8 : 1
 <b>197</b>	<i>i</i> -BuMgCl	96	10 : 1
 <b>198</b>	BnMgCl	96	10 : 1

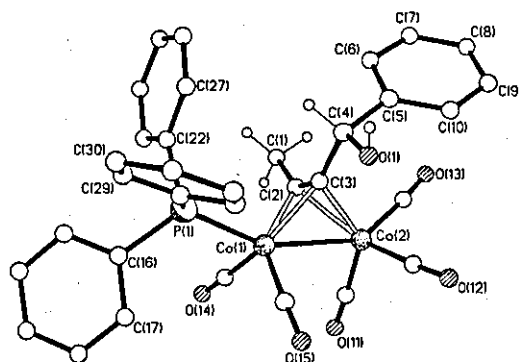
(Table 2 – Grignard addition to the heterobimetallic aldehyde complex)

X-Ray structures of the analogous desymmetrised *bis*-cobalt triphenylphosphine aldehyde **199** and the major phenyl Grignard product alcohol **200** were acquired by others in our group (Figure 4). On analysis of these structures, the metal centres were shown to be

perpendicular to the alkyne moiety. The aldehyde oxygen atom takes up a *syn* orientation towards the cobalt atoms, with one face being significantly blocked by the large triphenylphosphine ligand, seemingly opening up the opposite face for preferential nucleophilic attack. This was reflected in the reported diastereoselectivity of > 95% d.e.<sup>100</sup>



199

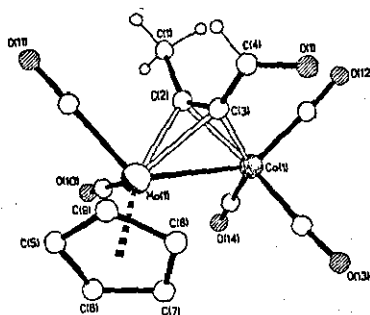


200

(Figure 4 - crystal structures of desymmetrised aldehyde and alcohol complexes)

An X-ray structure of the heterobimetallic aldehyde **186** could be obtained (Figure 5), although the obtained alcohol products could not be crystallised. Again, the metal centres were shown to be perpendicular to the alkyne moiety with the aldehyde oxygen atom taking up a *syn* orientation towards the two metal atoms, with one face being considerably blocked by the larger molybdenum cyclopentadienyl centre, leaving the opposite open face for preferential nucleophilic attack. The steric hindrance provided by the heterobimetallic system is reduced on comparison with the triphenylphosphine ligand and this is reflected in the lower diastereoselectivity achieved with the phenyl Grignard (69% d.e.). From analogy between the two aldehyde complexes, the same alcohol diastereoisomer is expected to be formed in preference, although there is no direct proof for this postulation.



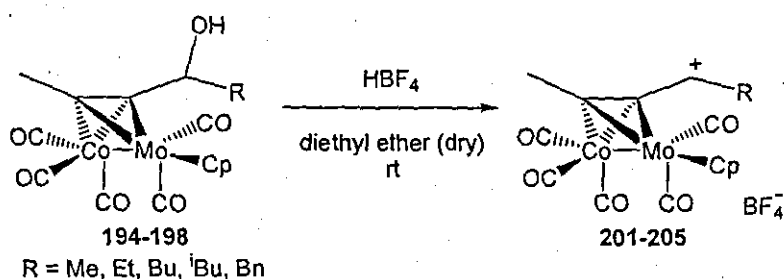


186

(Figure 5 - crystal structure of the heterobimetallic aldehyde)

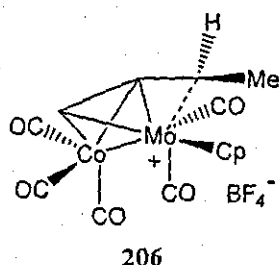
### 2.2.2 Synthesis of heterobimetallic Nicholas salts

Transition metal-stabilised propargylic salt complexes **201-205** can be formed by a variety of methods. Either treatment of complexed propargylic alcohols **194-198** and ethers with a Lewis acid, or addition of tetrafluoroboric acid ( $\text{HBF}_4$ ) to alcohol, ether or alkene complexes promotes loss of the leaving group or protonation of an alkene to create a positive charge at the propargylic position (Scheme 59). To be able to isolate the salt complexes, the propargylic alcohol complexes prepared above were protonated using  $\text{HBF}_4$ , with the positive charge at the propargylic position being stabilised by the metal complex and tetrafluoroborate acting as a counter ion.



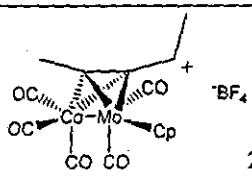
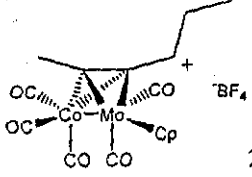
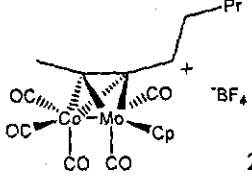
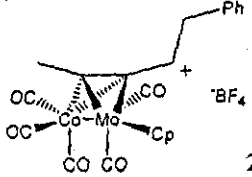
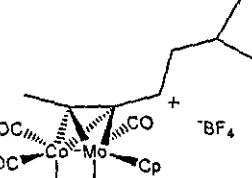
(Scheme 59 - synthesis of propargyl Nicholas salts)

It has been shown from the crystal structure of cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-but-2-yn-3-tetrafluoroborate **206**, that much of the positive charge is situated on the molybdenum centre, rather than on the cobalt with the propargylic position behaving more like an alkene and the propargylic carbon bending towards the molybdenum centre (Scheme 60).<sup>101, 102</sup>



(Scheme 60 – stabilisation of the positive charge by the molybdenum centre)

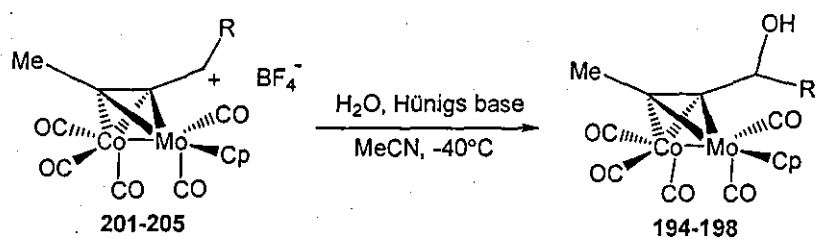
The propargyl Nicholas salts **201-205** were formed in generally very good yield (81-93%) (Table 3). The salts were generated by slow addition of  $\text{HBF}_4$  to the propargylic alcohol complexes under an atmosphere of nitrogen, at room temperature in dry diethyl ether, and precipitated as bright orange solids. Reactions were also performed at lower temperatures, but this had no effect on the yield. The salt complexes were subsequently filtered under suction and dried under vacuum, stored under an atmosphere of nitrogen at room temperature, or in the freezer ( $-18^\circ\text{C}$ ) for prolonged periods. The Nicholas salt complexes were not very soluble in most solvents, which is one reason that we were unable to acquire suitable  $^1\text{H}$  NMR spectroscopic data on these complexes, even though it has previously been reported by Gruselle et al.<sup>102</sup> Although spectra could be acquired, the peaks were extremely broad and a positive assignment was not possible. Accurate mass, IR and elemental analysis was consistent with the reported structures.

Salt complex	Yield (%)
 201	90
 202	81
 203	84
 204	93
 205	85

(Table 3 – synthesis of propargyl Nicholas salts)

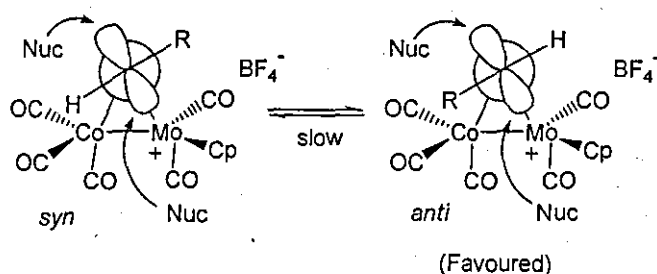
### 2.2.3 Nucleophilic addition to Nicholas salt complexes

Nucleophilic addition to the propargylic salt complexes **201-205** was initially examined using water in a variety of solvents and temperatures. Optimum conditions were found to be in acetonitrile at  $-40^{\circ}\text{C}$  in the presence of Hünigs base, with improvement of yields and diastereoselectivity at lower temperatures than at  $20^{\circ}\text{C}$  in acetonitrile (Table 4, Scheme 61). In the case of the benzyl substituted cation **204**, the alkene **207** was isolated rather than the alcohol **198**, presumably due to the stabilisation afforded by conjugation.



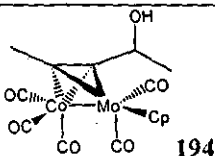
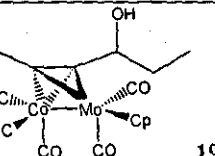
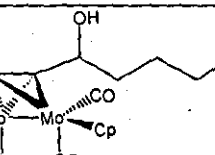
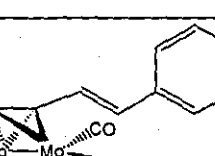
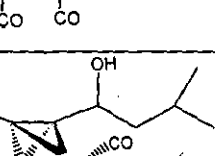
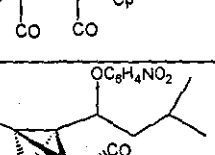
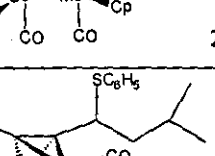
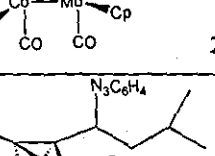
(Scheme 61 - nucleophilic addition to heterobimetallic salt complexes)

Interestingly, the relative d.r. of the created alcohol complexes **194-198** was reversed in comparison with the Grignard addition products to the heterobimetallic aldehyde complex **186**, thus enabling access to both of the alcohol diastereoisomers (61-70% yield, 3:1-6:1 d.r.), which were usually separable by column chromatography. This surprising result can be explained based on the difference in transition states for the two reactions. The aldehyde oxygen atom takes up a *syn* orientation towards the metal centre. Approach of the Grignard nucleophiles comes from the “cobalt” face rather than the “molybdenum” side. In the salt complex, nucleophilic attack from the least hindered face of the favoured rotamer of the cation, having the alkyl group *anti* to molybdenum, leads to the opposite alcohol diastereomer (Figure 6).



(Figure 6 - rationale for diastereoselectivity with heterobimetallic salt complexes)

As the highest diastereoselectivity and yield were found with the *iso*-butyl substrate **205**, nucleophilic additions with different heteroatoms were carried out using this propargylic salt complex.

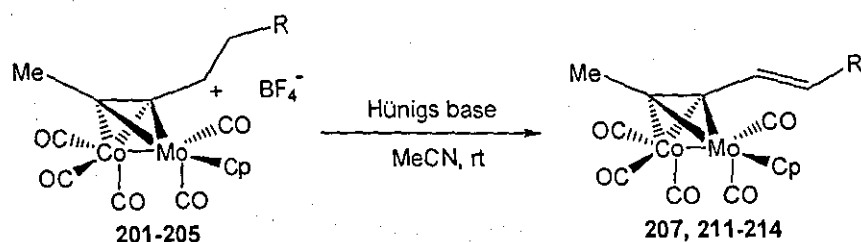
Nucleophile product	Nucleophile	Solvent	T (°C)	Yield (%)	d.r.
 194	H <sub>2</sub> O	MeCN	-40	68	3 : 1
 195	H <sub>2</sub> O	MeCN	-40	61	5 : 1
 196	H <sub>2</sub> O	MeCN	-40	66	4.5 : 1
 207	H <sub>2</sub> O	MeCN	-40	78	n/a
 197	H <sub>2</sub> O	MeCN	-40	70	6 : 1
 208		MeCN	25	58	1.5 : 1
	4-Nitrophenol	MeCN	-40	89	2 : 1
		Acetone	-78	88	1.5 : 1
 209		MeCN	25	90	2 : 1
	Thiophenol	MeCN	-40	93	4 : 1
		Acetone	-78	71	3.5 : 1
 210		MeCN	25	91	1 : 1
	1,2,3-Benzotriazole	MeCN	-40	95	3 : 1
		Acetone	-78	81	3 : 1

(Table 4 - nucleophilic addition to heterobimetallic salt complexes)

Excellent yields (89-95%) were achieved with the oxygen, sulfur and nitrogen nucleophiles of 4-nitrophenol, thiophenol and 1,2,3-benzotriazole under the optimised conditions; diastereoselectivity was moderate at room temperature but improved at  $-40^{\circ}\text{C}$  (2:1-4:1 d.r.). The diastereoisomers were not separable by standard column chromatography techniques and all products formed were oils. The relative diastereoselectivity was therefore confirmed using  $^1\text{H-NMR}$  spectroscopy.

#### 2.2.4 Using Nicholas methodology in the formation of enynes

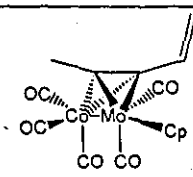
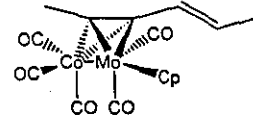
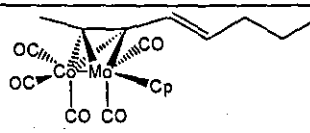
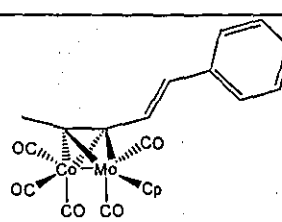
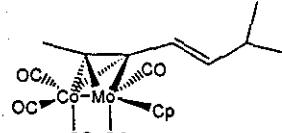
After the initial discovery of creating heterobimetallic enyne complexes on addition of base to Nicholas salts by A. J. Fletcher in our group, we decided to optimise this discovery and use them as possible substrates in subsequent 1,3-dipolar cycloaddition reactions. A range of different solvents and bases were investigated and the best method was found using *N*-ethyldiisopropylamine (Hünigs base) in dry acetonitrile at room temperature under an atmosphere of nitrogen (**Scheme 62**).



(Scheme 62 - creation of heterobimetallic enyne complexes)

Absolutely dry conditions were essential as the deprotonation reaction competes with the nucleophilic attack of any residual water in the reaction mixture. A series of enyne complexes 207, 211-214 has been created, generally in very good to excellent yield (83-94%) after standard column chromatography (**Table 5**). Reaction of the propargyl Nicholas salt complexes 201-205 with Hünigs base to form alkenes is an extremely fast process (1-10 min), with an almost immediate colour change from light orange/red to a dark burgundy, signalling the disappearance of the salt complex and generation of the

no increase in yield. The stereochemistry of the new alkene was found to be (*E*), as shown by  $^1\text{H}$  NMR coupling constants. This procedure creates enynes selectively masked at the alkyne functionality, i.e. with the alkene available for further conversions.

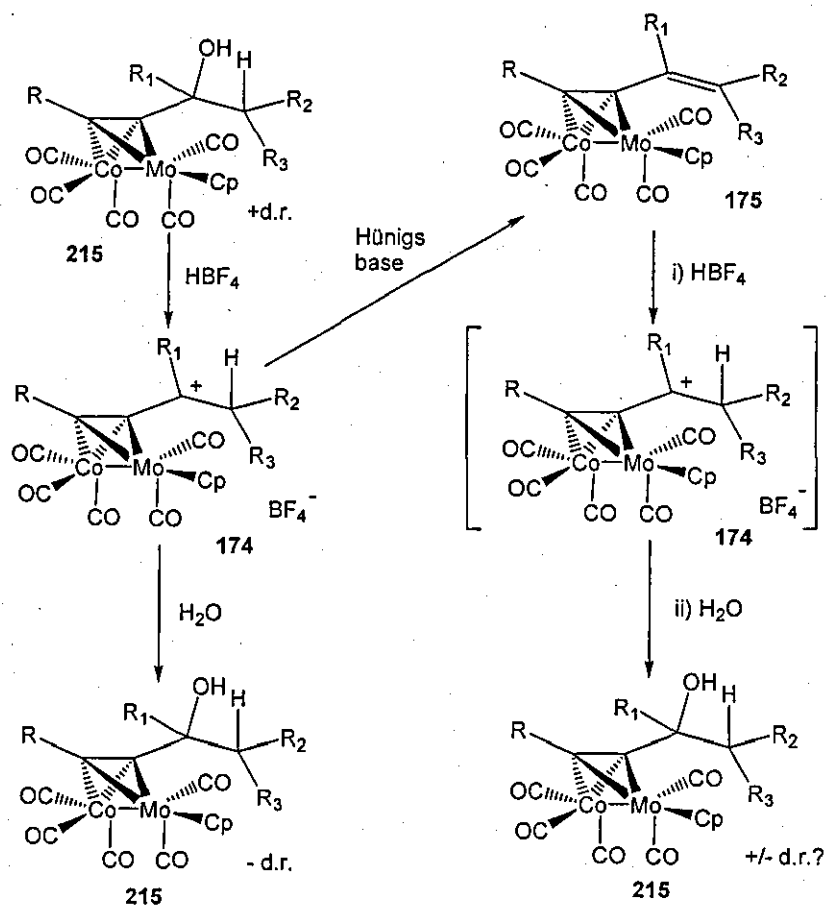
Olefination product	Yield (%)	Recovered alcohol (%)	d.r. of alcohol
 211	90	5	2 : 1
 212	94	1	5 : 1
 213	83	10	5 : 1
 207	94	0	n/a
 214	86	8	5 : 1

(Table 5 – synthesis of heterobimetallic enyne complexes from Nicholas salts)

### 2.2.5 Nucleophilic addition to protonated alkene complexes

Nucleophilic additions of water to heterobimetallic propargyl Nicholas salt complexes 201-205 have yielded d.r. reversed from the Grignard addition products, therefore offering access to both alcohol diastereoisomers. We were interested to establish whether nucleophilic addition after protonation of the alkenes 207, 211-214 prepared in the

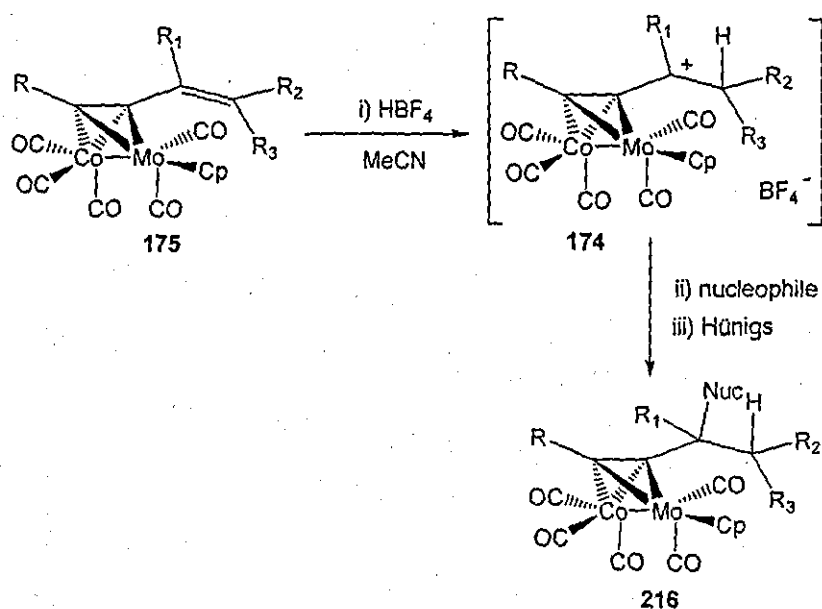
previous section had any effect on the yield or d.r. and which diastereoisomer was obtained in excess (**Scheme 63**).



(**Scheme 63** – comparison of nucleophilic addition from different routes)

After trials in a range of solvents, acetonitrile was found to be the solvent of choice for these *in situ* reactions.  $\text{HBF}_4$  protonated the alkene at ambient temperature and Hünigs base was added to finally drive the reaction after addition of the nucleophile (**Scheme 64**). Initially water was used as the nucleophile, thus acting as a direct comparison to addition to the salt complexes **201-205**. The more nucleophilic methanol was also used to see if higher yields could be obtained by this method and since it is larger than water it may give a modified diastereomeric ratio.

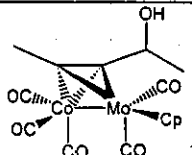
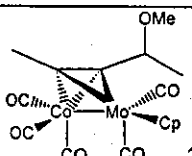
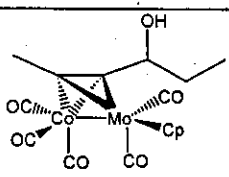
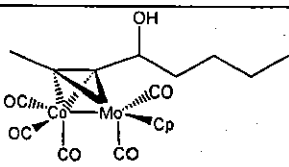
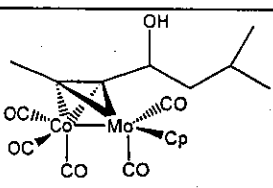
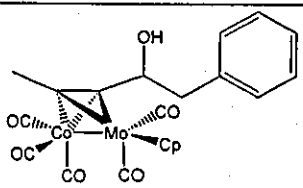




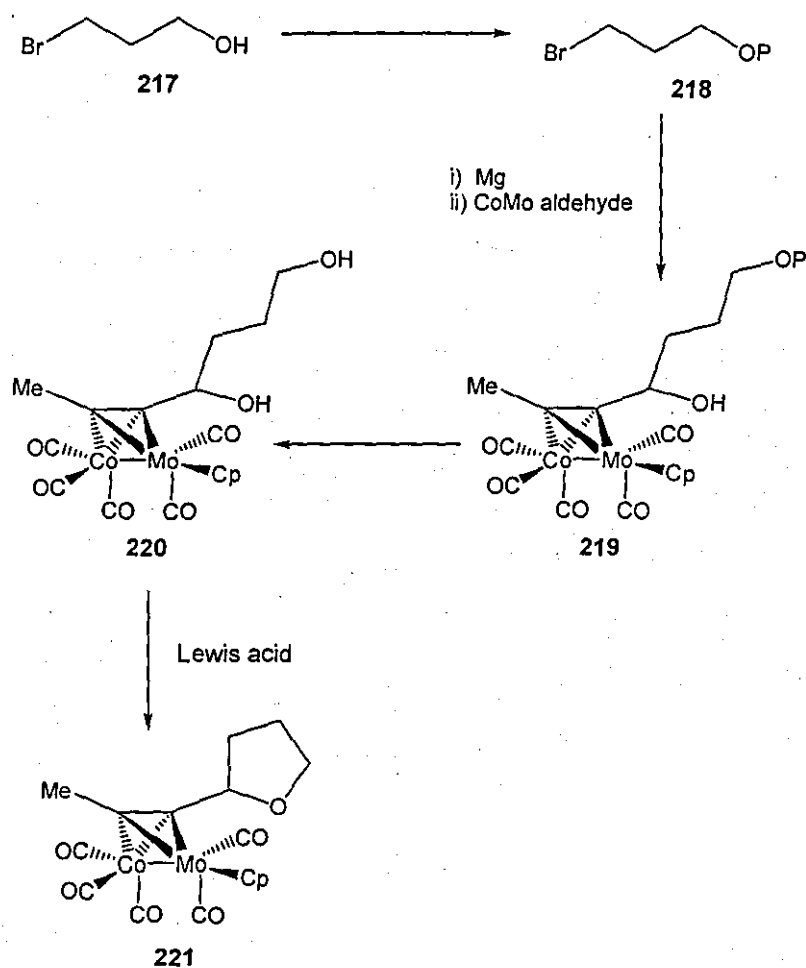
(Scheme 64 – *in situ* nucleophilic addition to propargyl Nicholas complexes from alkenes)

Nucleophilic addition to alkenes *via in situ* synthesis of the propargyl Nicholas cation proceeded in similar diastereomeric ratios as from the salt complexes and with equivalent yields (Tables 4 and 6), therefore supporting reaction through an identical transition state. Yields with water were good (59-66%), but nucleophilic addition into the styryl complex 207 showed an unusual result. The complexes were decomposing on rotary evaporation after purification, with some evidence for benzylic addition products also being formed from the crude  $^1\text{H}$  NMR spectra. This is possibly due to the stabilising effect of the phenyl ring on that position, enabling competition from nucleophilic addition at both sites. However it seems both products are unstable and isolation proved difficult. In comparison to creation of the enyne on addition of water to the propargylic salt complex, this substrate does not follow the same pattern as other alkyl substituents. As  $\text{HBF}_4$  is present in protonation of the alkene, it protonates at either end to give two stabilised cations to which water can be added. Upon reaction of the methyl substituted cation 201 with methanol the yield increased to 85% with a 2:1 d.r., which is most likely due to a faster reaction and reducing decomposition products. Recovery of the alkene

starting material was high in some cases, showing a competition between loss of a proton and capture of nucleophile by the propargyl cation complex under these conditions.

Nucleophile product	Nucleophile	Yield (%)	d.r.	Recovered alkene (%)
 194	H <sub>2</sub> O	59	2 : 1	40
 217	MeOH	85	2 : 1	10
 195	H <sub>2</sub> O	61	5 : 1	15
 196	H <sub>2</sub> O	66	5 : 1	6
 197	H <sub>2</sub> O	65	5 : 1	25
 198	H <sub>2</sub> O	30	1 : 1	37

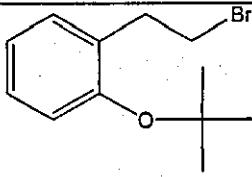
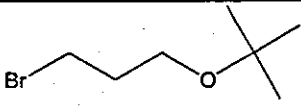
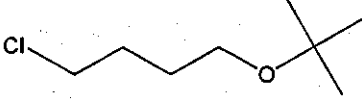
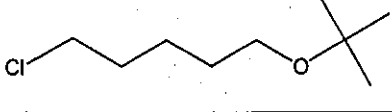
(Table 6 – *in situ* nucleophilic additions to propargyl Nicholas complexes from alkenes)



(Scheme 65 – initial route for intramolecular nucleophilic addition)

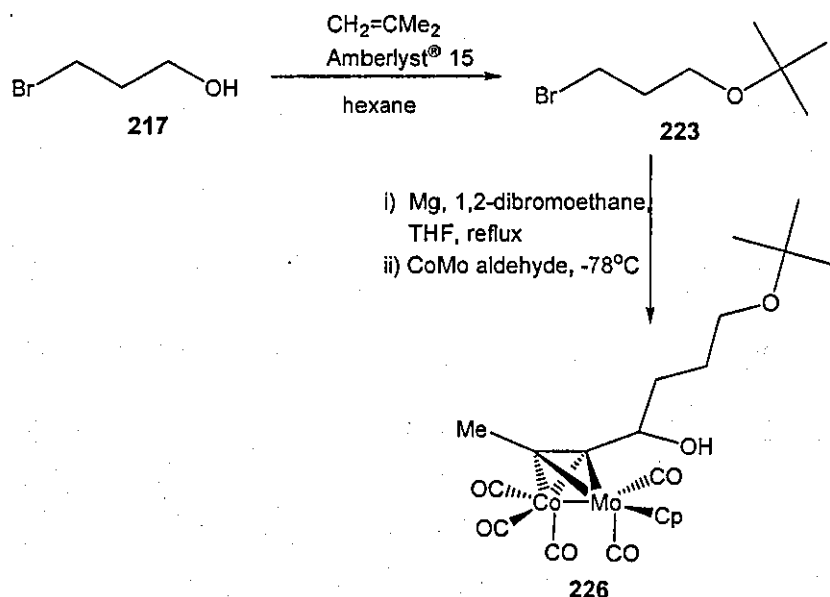
The first stage of this synthesis was protection of the alcohol with a substituent that would enable formation of a Grignard reagent. The first group we trialled was tetrahydropyranyl, from an acid catalysed reaction with 2,3-dihydropyran, isolating the desired product in 88% yield. Attempts to form the Grignard reagent from this product were ineffective under a series of conditions, including using iodine, 1,2-dibromoethane and a few drops of MeMgBr as initiators in both diethyl ether and THF as solvents. As a result we turned to a *tert*-butyldimethylsilyl protecting group, which also failed under similar attempts. Eventually, after searching the literature for suitable protecting groups in Grignard synthesis the use of a *tert*-butyl ether was found.<sup>103</sup> Subsequent protection of 3-bromopropan-1-ol 217 by treatment with 2-methylpropene over the acidic Amberlyst®

15 in hexane fashioned the *tert*-butyl ether **223**, which finally enabled generation of the Grignard reagent, therefore a series of protections of various bi-terminal halogen alcohols **222-225** was performed (Table 7).

Protected alcohol	Yield (%)
 222	54
 223	89
 224	82
 225	81

(Table 7 – alcohol protection as *tert*-butyl ethers)

The *tert*-butyl ether was prepared by bubbling 2-methylpropene into a flask fitted with a cold trap ( $-78^{\circ}\text{C}$ ,  $\text{CO}_2(\text{s})/\text{acetone}$ ), containing 3-bromopropan-1-ol and Amberlyst<sup>®</sup> 15 in hexane, isolating the desired product in 89% yield. To generate the Grignard reagent, magnesium was freshly washed with acid, water, acetone and diethyl ether. The clean, dry material was added to a flame-dried Schlenk flask, followed by addition of dry THF and a few drops of 1,2-dibromoethane. The *tert*-butyl ether **223** in dry THF was then added and the solution refluxed until disappearance of the magnesium was evident. At this point the solution was cooled to  $-78^{\circ}\text{C}$ , subsequently adding the heterobimetallic aldehyde **186** in THF and the reaction was stirred for 2.0 h at  $-78^{\circ}\text{C}$ , isolating the corresponding heterobimetallic alcohol **226** in 89% yield and in 7:1 d.r. (Scheme 66). The equivalent method was applied to the other haloalcohol substrates.

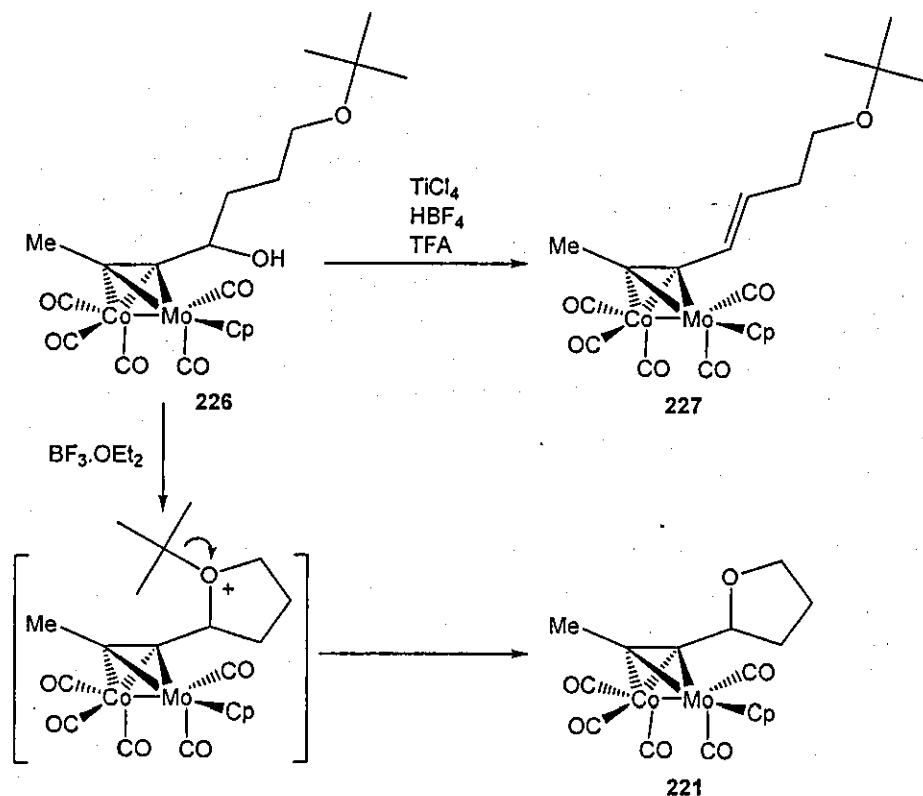


(Scheme 66 – synthesis of heterobimetallic tetrahydrofuran precursor)

### 2.3.2 Cyclisation using Nicholas methodology

Upon formation of the heterobimetallic tetrahydrofuran precursor **226**, a series of Lewis acids was trialled to remove the *tert*-butyl ether protecting group and propargylic alcohol in a single step, thus enabling ring closure to occur (Scheme 67). TFA,  $\text{TiCl}_4$  and  $\text{HBF}_4$  all produced the corresponding enyne complex **227** in varying yields (70, 25, 50%) on dehydration of the alcohol, leaving the protecting group intact. However, on reaction with  $\text{BF}_3\cdot\text{OEt}_2$  in DCM the heterobimetallic tetrahydrofuran **221** was produced in 40% yield. On addition of three equivalents of  $\text{BF}_3\cdot\text{OEt}_2$  in DCM at  $-78^\circ\text{C}$  the yield rose to 79% and the product formed in a 2:1 d.r. Interestingly, reaction in acetonitrile at  $-40^\circ\text{C}$  only yielded the enyne product in 49%. In an attempt to increase the d.r.,  $\text{BF}_3\cdot\text{OEt}_2$  was added to the preformed heterobimetallic furan **221** in DCM at  $-78^\circ\text{C}$ , as an equilibrium should establish as the Lewis acid opens and closes the ring. Taking the furan in both 1:1 and 2:1 d.r. they were reacted separately and stirred for 1.0 h, after this time isolation revealed they both formed in 2:1 d.r., suggesting that this is the optimum thermodynamic d.r. under these conditions. As the *tert*-butyl ether protecting group is still present on the

dehydrated enynes, it is possible that it is removed only after ring closure has occurred, with the driving force to quench the oxygen cation aiding cleavage.

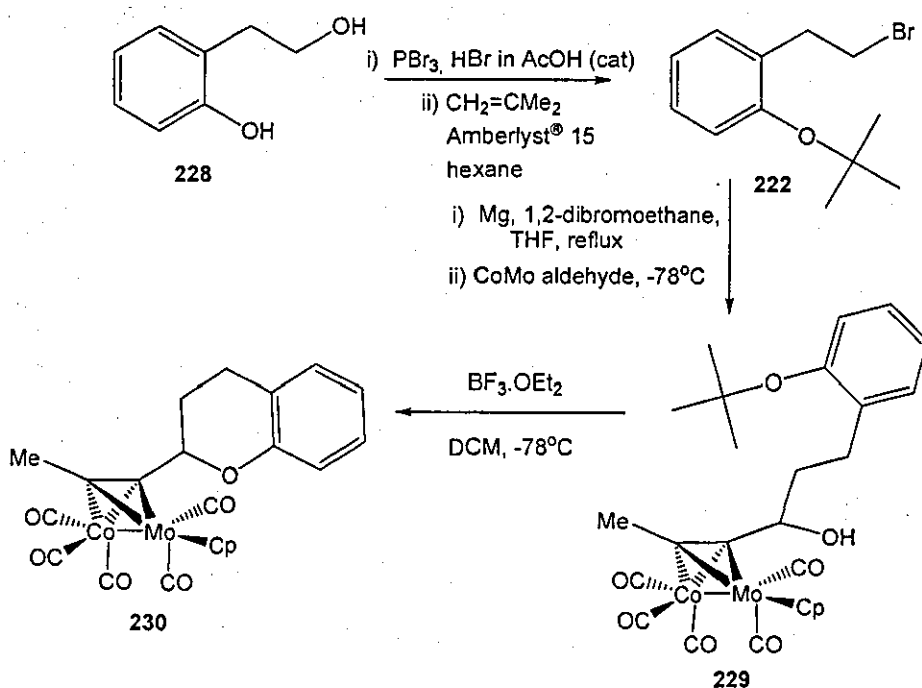


(Scheme 67 – Lewis acid addition to the heterobimetallic tetrahydrofuran precursor)

Synthesis of the six-membered pyran ring equivalent did not yield such success. The pyran precursor was created in 82% yield and 3:1 d.r. in an analogous Grignard addition to the heterobimetallic aldehyde 186. Unfortunately, addition of the Lewis acid mostly fashioned the enyne product (49%), with a minor product resembling the pyran but with the *tert*-butyl peak still evident in the  $^1\text{H}$  NMR spectrum. We hypothesise that the extra carbon reduces the probability of ring closure, and dehydration is a more favourable process. Therefore an increase in substitution should encourage ring closure by restricting the conformational flexibility and we moved to attempting a dihydrobenzopyran synthesis (Scheme 68).

### 2.3.3 Application to a carbenoid precursor

After formation of the heterobimetallic furan complex **221**, it was found that a propargylic ether centre in a six-membered ring is a common core in alkaloid molecules. This correlated directly to the Nicholas methodology we had been investigating, therefore we designed a pilot study of six-ring formation in making an unsubstituted dihydrobenzopyran **230**, extending from failed attempts without the benzyl group present (Scheme 68).



(Scheme 68 – synthesis of a heterobimetallic propargyl dihydrobenzopyran)

Following a similar route to the furan synthesis (Scheme 67) we initially attempted bromination of the primary alcohol of 2-(2-hydroxyphenyl)ethanol **228** with  $\text{PBr}_3$  and catalytic  $\text{HBr}$  in acetic acid, stirring for 40.0 h to yield 2-(2-hydroxyphenyl)bromoethane, 49%. Protection of the phenol as the *tert*-butyl ether **222** yielded only 54% product, a decrease of 30% from the earlier protections, but generation of the Grignard reagent was successful and subsequent addition to the heterobimetallic aldehyde furnished the pyran

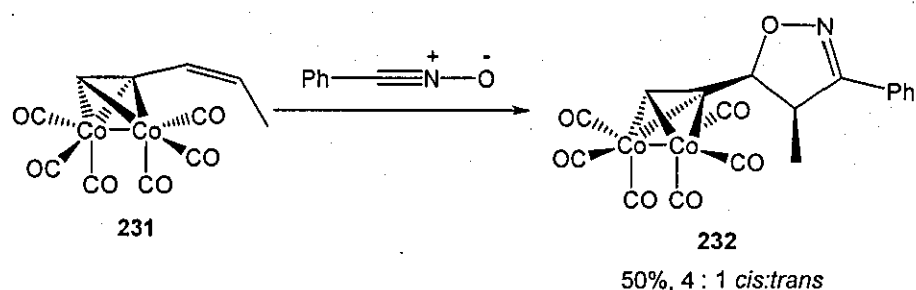
precursor **229** in 75% yield and 7:1 d.r. The cyclisation was completed on treatment with  $\text{BF}_3 \cdot \text{OEt}_2$  in DCM at  $-78^\circ\text{C}$ , but unfortunately only in 20% yield and 2:1 d.r., although this was not studied further due to the small amounts of material available. Further work will be necessary to optimise this process.



## 2.4 1,3-Dipolar cycloadditions with bimetallic systems

### 2.4.1 Background

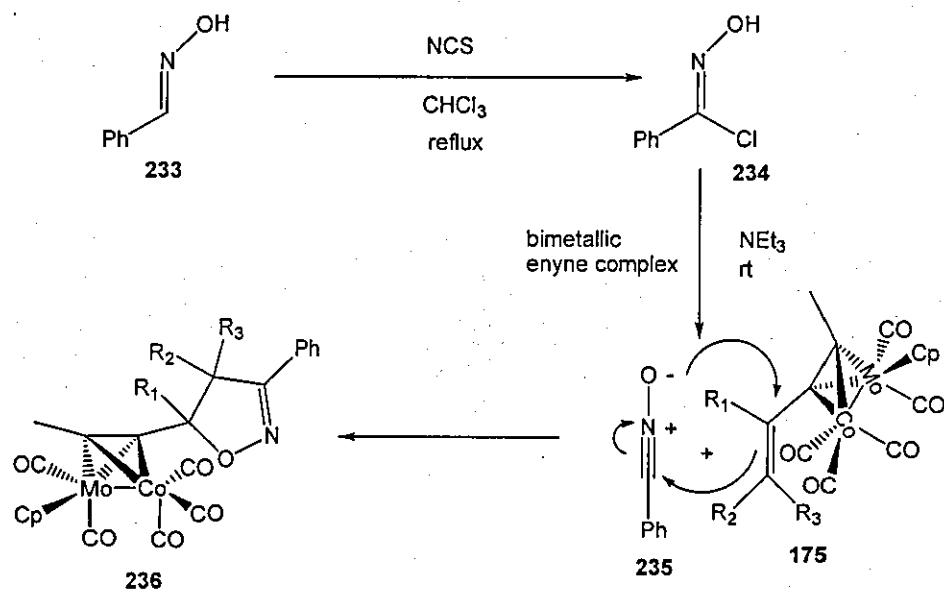
It has been previously reported in the literature that 1,3-dipolar cycloadditions can occur regio- and stereoselectively using dicobalt hexacarbonyl enyne complexes.<sup>97</sup> Therefore, upon utilising an inherently chiral heterobimetallic system such as the cobalt-molybdenum alkyne complexes, it may be possible to induce enantioselectivity and increase diastereoselectivity in the products formed. The reported homobimetallic enyne complexes were treated with nitrile oxide 1,3-dipoles with exclusive regiochemistry, with the bulky R-group in the dipole and homobimetallic group on the enyne residing at C-3 and C-5 of the isoxazoline. Whilst this minimises the steric effects of the two large groups on the substrates, the regioselectivity also agrees with the electronic preference, maximising frontier orbital overlap of the polarity matched 1,3-dipole and stabilisation of the Nicholas carbocation by the *bis*-cobalt metal complex. Cycloaddition using a (*Z*)-enyne **231** fashioned the isoxazoline **232** with preference for retained stereochemistry, with the product showing a 4:1 mixture of *cis*- and *trans*-isomers. This is also consistent with general dipolar cycloadditions (Scheme 69). Nicholas also found that yields were reduced on using sterically more hindered systems.



(Scheme 69 – dipolar cycloaddition with retention of stereochemistry)

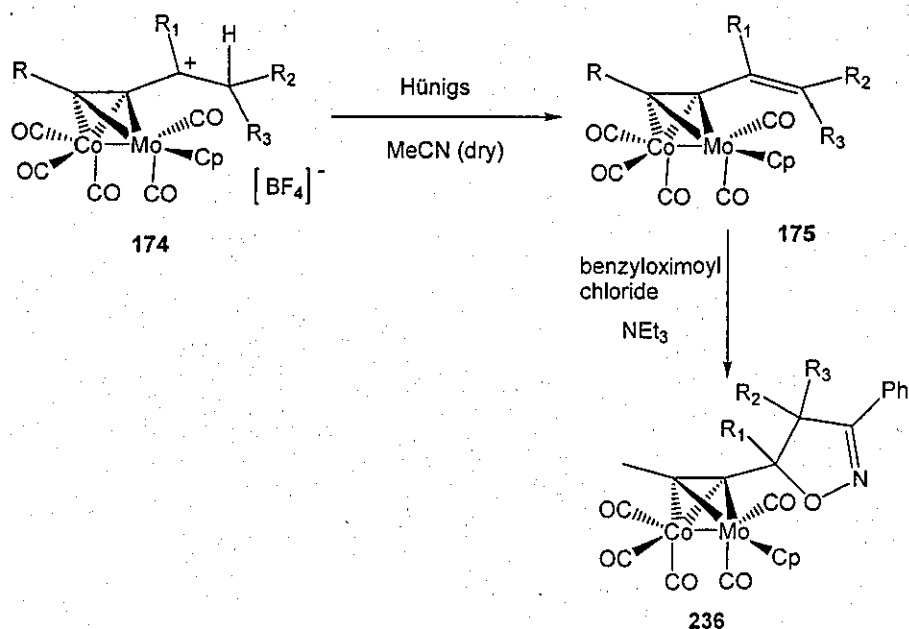
The nitrile oxide cycloadditions of enyne bimetallic carbonyl complexes were carried out by initially forming the hydroximoyl chloride **234** of benzaldehyde oxime **233**, on refluxing in chloroform with *N*-chlorosuccinimide. After cooling to room temperature the

enyne bimetallic carbonyl complex **175** was added, with formation of the dipole **235** *in situ* upon slow addition of triethylamine. The reaction was followed by TLC (Scheme 70).



(Scheme 70 – a general 1,3-dipolar cycloaddition)

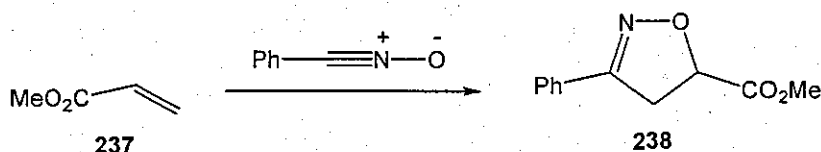
The discovery of the formation of heterobimetallic enyne complexes **207**, **211-214** created from Nicholas stabilised propargyl salt complexes **201-205** after treatment with base, provided us with a range of substrates to react with 1,3-dipoles (Scheme 71). Our primary research was carried out on homobimetallic systems, thus being a direct comparison to the work reported by Nicholas et al.<sup>97</sup>



(Scheme 71 – general enyne formation, followed by cycloaddition)

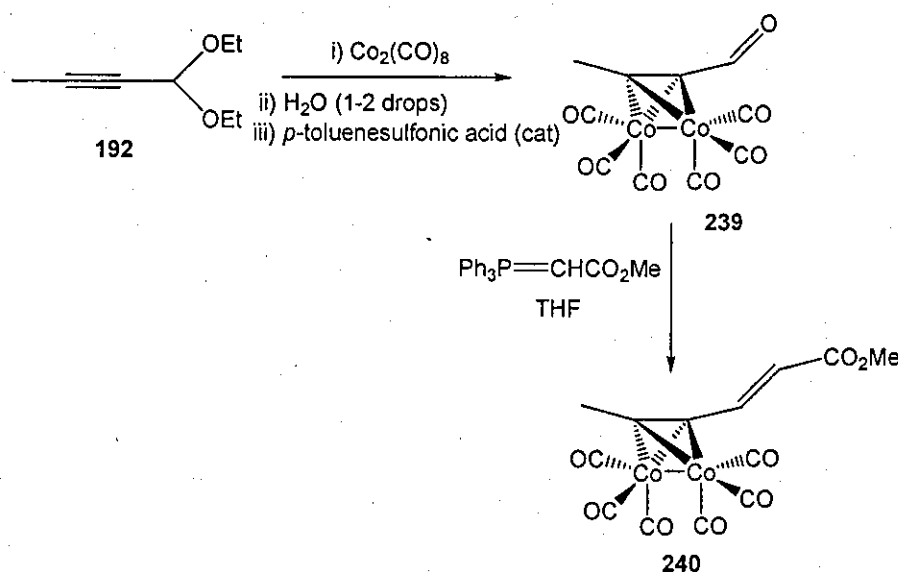
#### 2.4.2 Homobimetallic 1,3-dipolar cycloadditions

Our primary objective was to try nitrile oxide 1,3-dipolar cycloadditions on two different enyne dicobalt hexacarbonyl complexes **240** and **243**, after an initial test reaction using benzaldehyde oxime as source of the dipole, and methyl acrylate **237** to create methyl 3-phenyl-4,5-dihydroisoxazole-5-carboxylate **238** was achieved in 50% yield to validate the protocol used. The enynes were selected to have an electron deficient and an electron rich alkene unit (Scheme 72).



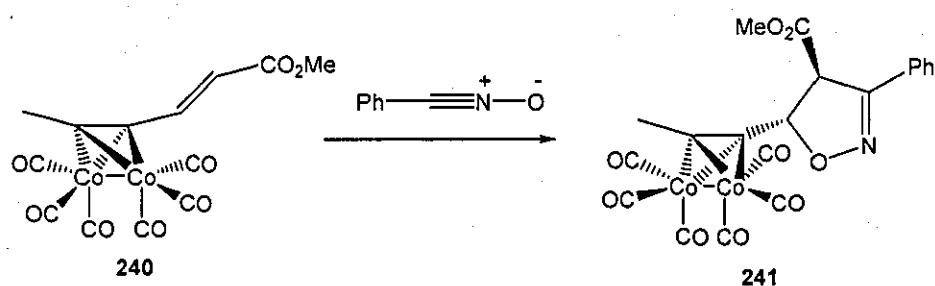
(Scheme 72 – a test dipolar cycloaddition with methyl acrylate)

The first enyne, dicobalt hexacarbonyl-methyl (*E*)-hex-2-en-4-ynoate **240** was formed by taking 2-butynal diethyl acetal **192**, complexing with dicobalt octacarbonyl and hydrolysing to the aldehyde **239** by treatment with water and *p*-toluenesulfonic acid with loss of ethanol, overall in 85% yield. Dicobalt hexacarbonyl-butynal **239** was then converted to dicobalt hexacarbonyl-methyl-(*E*)-hex-2-en-4-ynoate **240** using a Wittig reaction by treatment with stabilised ylid of methoxycarbonylmethyltriphenylphosphonium bromide. This was fashioned by treatment of the salt with sodium hydroxide in water and extracting the ylide into DCM, concentrating *in vacuo* and re-dissolving in dry THF. On addition of the aldehyde complex **239** and stirring overnight dicobalt hexacarbonyl-methyl-(*E*)-hex-2-en-4-ynoate **240** was obtained in a 91% yield (Scheme 73).



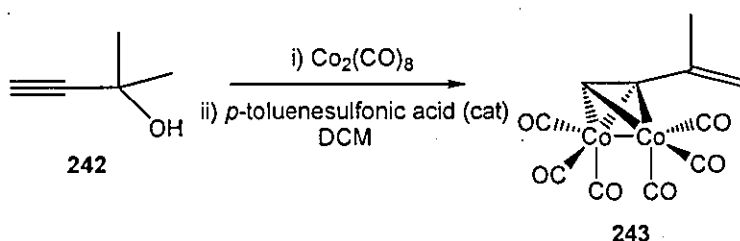
(Scheme 73 – formation of dicobalt hexacarbonyl-methyl-(*E*)-hex-2-en-4-ynoate)

Initial cycloadditions using one equivalent of benzonitrile oxide only fashioned the target isoxazoline in approximately 25% yield. When an excess of dipole (3 equivalents) was used and conditions optimised the yield increased to 57% (Scheme 74). A single regioisomer was created, which from analogy of the steric and electronic effects referred to earlier we believe to be isoxazoline **241**.



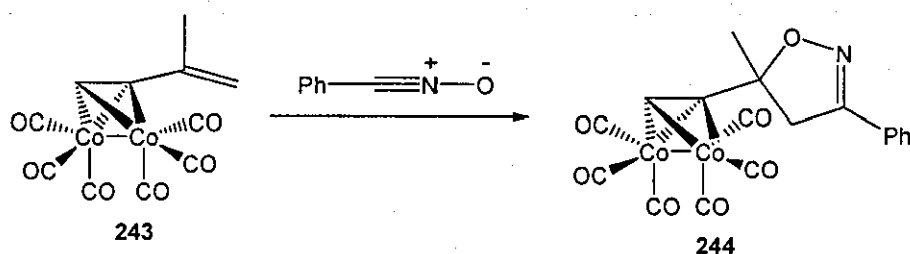
**(Scheme 74 – initial cycloaddition using benzonitrile oxide)**

The second enyne, dicobalt hexacarbonyl-2-methylbut-1-en-3-yne **243** was formed by complexation and subsequent loss of water from 2,2-dimethyl-3-butyn-2-ol **242**. The reaction was catalysed using *p*-toluenesulfonic acid in 75% yield, although when taking pre-complexed 2,2-dimethyl-3-butyn-2-ol, yields of up to 90% can be achieved (**Scheme 75**).



**(Scheme 75 – formation of dicobalt hexacarbonyl-2-methylbut-1-en-3-yne)**

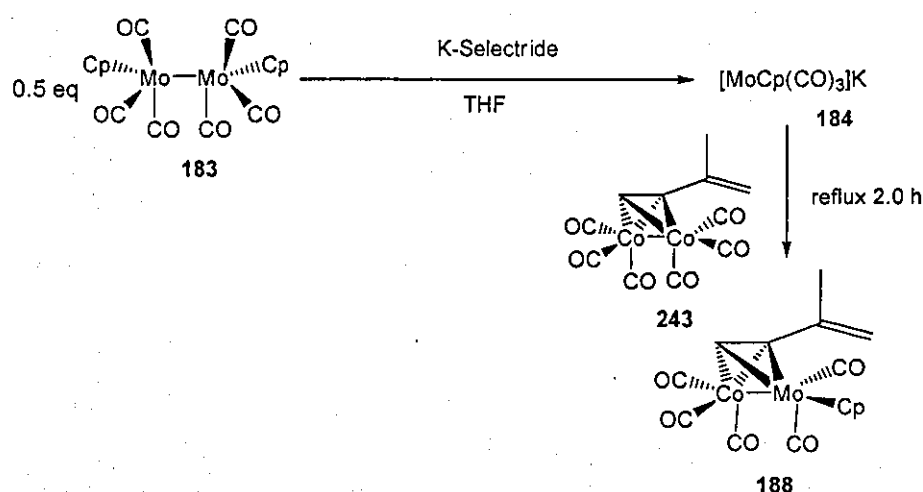
Again, initial cycloaddition with one equivalent of benzonitrile oxide only formed a single regioisomer of dicobalt hexacarbonyl-5-ethynyl-5-methyl-3-phenyl-4,5-dihydroisoxazole **244** in 25% yield. With an excess of dipole and conditions optimised the yield increased to 91% (compare the 80% reported by Nicholas),<sup>97</sup> a great improvement from the previous enyne (**Scheme 76**). This provided us with the confidence to attempt cycloadditions on heterobimetallic cobalt-molybdenum systems, as a 91% yield indicates the conditions are sufficiently optimised.



(Scheme 76 – cycloaddition with dicobalt hexacarbonyl-2-methylbut-1-en-3-yne)

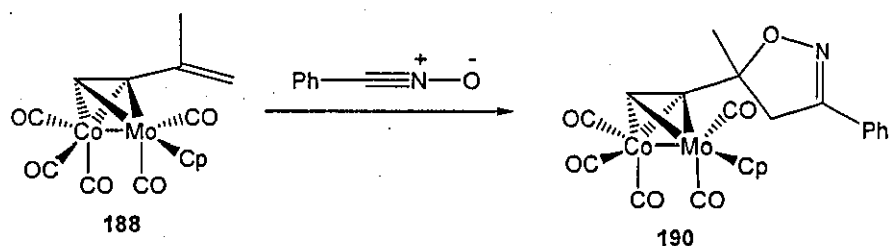
### 2.4.3 Heterobimetallic 1,3-dipolar cycloadditions

The first isolobal displacement of cobalt tricarbonyl for cyclopentadienyl molybdenum dicarbonyl was carried out on dicobalt hexacarbonyl-2-methylbut-1-en-3-yne **243**. The initial step of this reaction was to use K-Selectride to cleave the molybdenum cyclopentadienyl dimer **183**, creating two molybdenum cyclopentadienyl tricarbonyl anions **184**. This was carried out by dissolving half an equivalent of molybdenum cyclopentadienyl dimer **183** in dry THF under a nitrogen atmosphere, subsequently adding 2.5 equivalents of K-Selectride and stirring for 1.0 h. Loss of hydrogen gas subsided as the anion was being formed. This methodology has already been discussed (Pages 54-55). Dicobalt hexacarbonyl-2-methylbut-1-en-3-yne **243** was then added and the reaction mixture was refluxed for 2.0 h, following the reaction by TLC to yield 70% of the displaced product (Scheme 77).



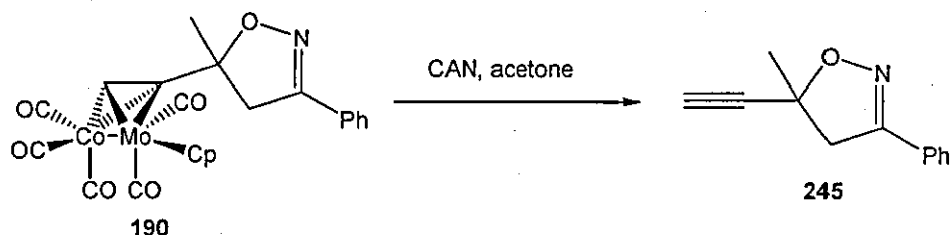
(Scheme 77 – isolobal displacement of dicobalt hexacarbonyl-2-methylbut-1-en-3-yne)

When a 1,3-dipolar cycloaddition with benzonitrile oxide was attempted on cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-2-methylbut-1-en-3-yne **188** it was very difficult to detect any product by TLC. Therefore, the product was verified by an alternate synthesis *via* isolobal displacement of the preformed dicobalt hexacarbonyl-5-ethynyl-5-methyl-3-phenyl-4,5-dihydroisoxazole **190**. This was carried out with L-Selectride and the molybdenum dimer **183** in 25% yield and 1:1 d.r., which later improved to 40% yield upon treatment with K-Selectride. During subsequent cycloadditions, the products were found and isolated as a 1:1 mixture of two diastereoisomers. These diastereoisomers were separated by flash silica chromatography eluting in petroleum ether-diethyl ether (15:1) as a 4:3 mixture in 49% yield (Scheme 78), plus a minor impurity. Duplicate reactions gave very similar results, in approximately 1:1 d.r., therefore showing the heterobimetallic core was having little to no influence over which diastereoisomer was being created, although in this case the differentiation was only between a methyl and terminal alkene group, so a poor d.r. was not unexpected.



(Scheme 78 – 1,3-dipolar cycloaddition with cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-2-methylbut-1-en-3-yne)

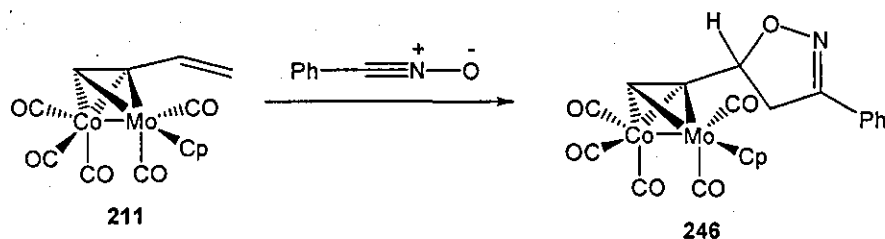
In order to purify the product further, the metal complex was removed from the second eluting diastereoisomer using 3 equivalents of ceric ammonium nitrate, releasing carbon monoxide during oxidation of the metal complex to yield an off-white solid (**Scheme 79**). Upon column chromatography the product was not entirely purified, but on recrystallisation in *n*-hexane the pure isoxazoline **245** was isolated in 21% overall yield.



(Scheme 79 – removal of the heterobimetallic core with ceric ammonium nitrate)

After achieving little or no diastereoselection between the methyl and methylene groups on reacting cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-2-methylbut-1-en-3-yne **188** we decided to investigate if a d.r. could be attained with differentiation between a proton and a methylene group, from reaction of cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-but-1-en-3-yne **211** with benzonitrile oxide (**Scheme 80**).



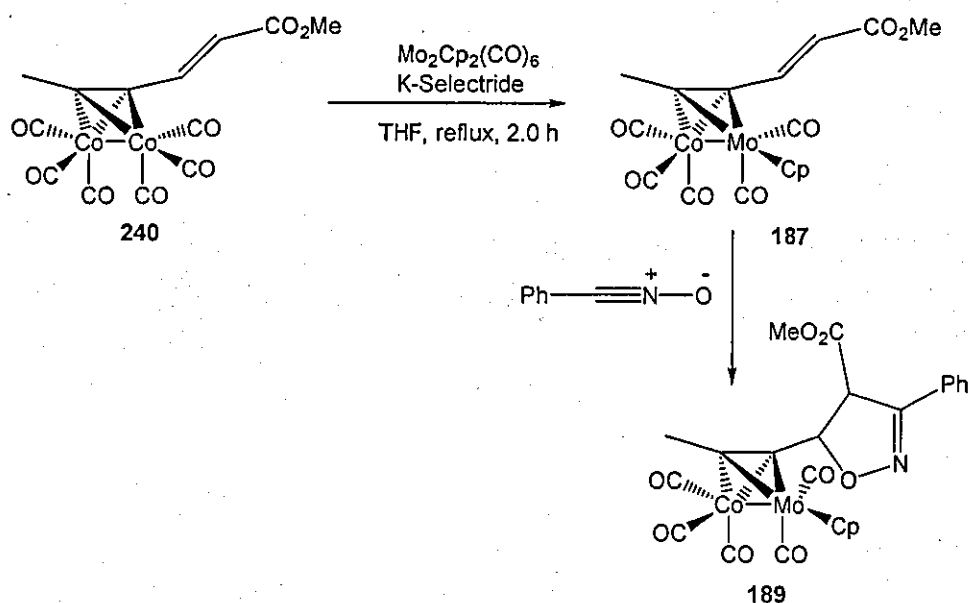


(Scheme 80 – 1,3-dipolar cycloaddition with cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-but-1-en-3-yne)

An increase in yield was expected owing to the decrease in steric hindrance, along with some diastereoselection between the methylene and proton group. The required cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-5-ethynyl-3-phenyl-4,5-dihydroisoxazole **246** was isolated in 49% yield, but unfortunately in 1:1 d.r. This result posed the question of how the dipole approaches the enyne and the conformation of the enyne during attack. The dipole is probably not approaching *via* the metal complex, even though the oxygen nucleophile attacks the propargylic carbon, or at least is not influenced by the differentiation of the two metal centres. The alkene could also be freely rotating about the ene-yne bond and not fixed as in the example of Grignard additions to the heterobimetallic aldehyde mentioned earlier (**Figure 5**), where diastereoselectivity of up to 10:1 d.r. was achieved (**Table 2**), or on addition to the Nicholas propargylic salt complexes, where with an analogous methyl substituent a 3:1 d.r. was created on addition of water (**Table 4**).

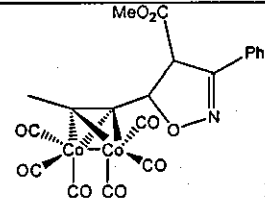
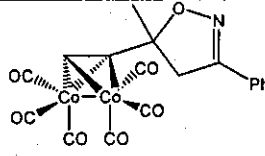
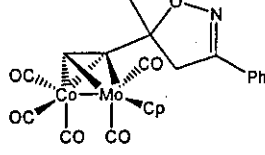
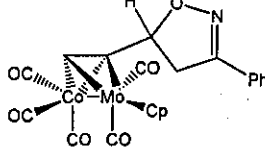
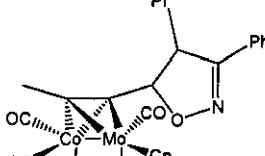
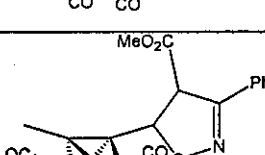
Following the previous dipolar cycloaddition results, reaction with the heterobimetallic enyne ester was of interest. Isolobal displacement was carried out on dicobalt hexacarbonyl-methyl-(*E*)-hex-2-en-4-ynoate **240** in 75% yield, but cycloaddition on this complex was unsuccessful, affording the desired complex **189** in only 7% yield and in 1:1 d.r. (**Scheme 81**). The significant reduction in yield could be due to the increase in steric bulk of the heterobimetallic system and the decrease in reactivity of the alkene as the molybdenum cyclopentadienyl centre is more electron rich than the cobalt group. The target isoxazoline can be obtained from isolobal displacement of the corresponding

homobimetallic equivalent, but again in only 40% yield and 1:1 d.r., a result identical to the dicobalt hexacarbonyl-2-methylbut-1-en-3-yne example.



(Scheme 81 – isolobal displacement of dicobalt hexacarbonyl-methyl (*E*)-hex-2-en-4-ynoate followed by 1,3-dipolar cycloaddition)

1,3-Dipolar cycloadditions of benzonitrile oxide have been attempted on a range of heterobimetallic complexes but with limited success, a summary of results is shown here (Table 8).

Product	Yield (%)	d.r.	s/m (%)
 241	57	n/a	32
 244	91	n/a	3
 190	49	4 : 3	15
 246	55	1 : 1	11
 247	0	0	25
 189	7	1 : 1	44

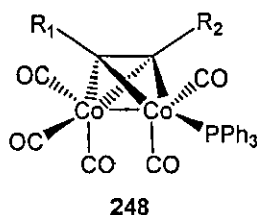
(Table 8 – 1,3-dipolar cycloaddition of bimetallic enyne complexes)

Poor yields with more sterically hindered alkenes made it difficult to accurately assess the influence the heterobimetallic core has on the 1,3-dipolar cycloaddition. This is consistent with the research reported by Nicholas,<sup>97</sup> where yields decrease on more sterically hindered systems. Even reacting at  $-40^{\circ}\text{C}$  with cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-but-1-en-3-yne **211** did not improve on the 1:1 d.r. from the equivalent

reaction at room temperature, only decreasing the yield to 42%. This result was very significant as it shows at lower temperatures the equilibrium of alkene conformations has not been affected, raising the hypothesis that the bond may be freely rotating and not effected by the metal core at all. One positive influence from using the heterobimetallic system is that the diastereoisomers formed can be separated and isolated. However, due to the disappointing results no further work was carried out with these systems and a different desymmetrised system was attempted.

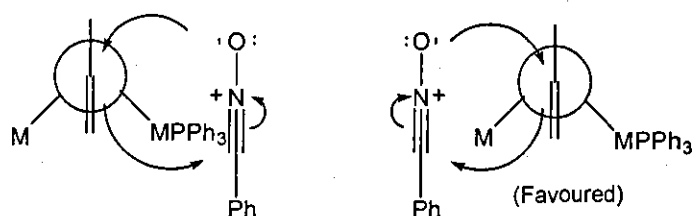
#### 2.4.4 Desymmetrised 1,3-dipolar cycloadditions

After the moderate success described above with the heterobimetallic cobalt-molybdenum system, it was decided to try a different unsymmetrical system, with a mono-substituted triphenylphosphine ligand on one of the cobalt centres, creating a desymmetrised dicobalt pentacarbonyl triphenylphosphine complex **248** (Scheme 82).



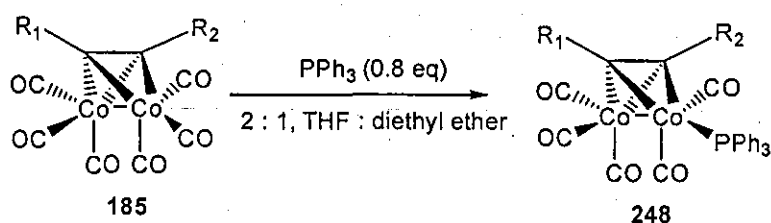
(Scheme 82 - a dicobalt pentacarbonyl triphenylphosphine complex)

Dicobalt pentacarbonyl triphenylphosphine complexes are made *via* substitution of a triphenylphosphine ligand for a carbon monoxide ligand. This metal system has similar electronics to the cobalt-molybdenum system, as the triphenylphosphine ligand donates electron density into the metal core. The difference between the complexes is a greater steric influence from the larger triphenylphosphine ligand. This decreases the probability of the dipolar attack from the substituted face, thus increasing the potential for diastereoselectivity, but with the possibility of the alkene complex being too sterically hindered for attack to occur (Scheme 83).



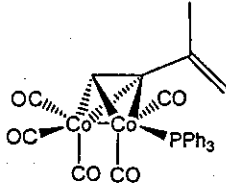
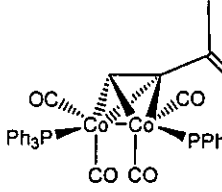
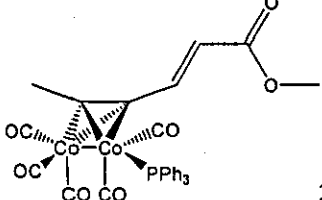
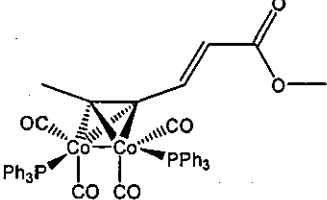
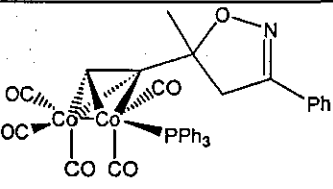
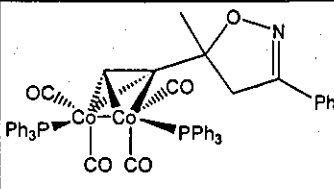
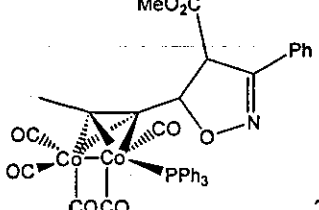
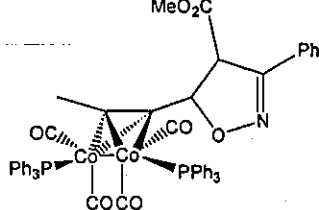
(Scheme 83 – theoretical influence of the triphenylphosphine ligand)

These complexes were made from dropwise addition of 0.8 equivalents of triphenylphosphine in a 2:1 mixture of THF:diethyl ether to the dicobalt hexacarbonyl complex **185** in a 2:1 mixture of THF:diethyl ether at 50°C over 1.5 h, stirring until no triphenylphosphine was present by TLC (Scheme 84).



(Scheme 84 – phosphination of a dicobalt hexacarbonyl complex)

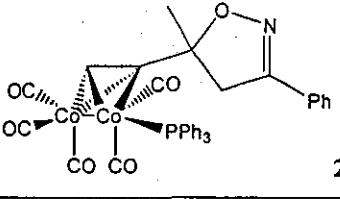
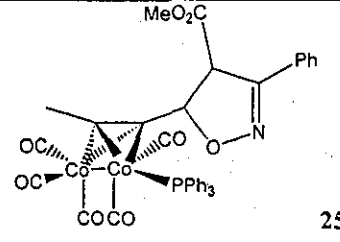
0.8 Equivalents of triphenylphosphine were used to minimise the amount of the diphosphinated by-product produced, whereby a triphenylphosphine ligand displaces a carbon monoxide ligand on each of the two cobalt centres, creating an unwanted achiral system. Phosphination of dicobalt hexacarbonyl complexes was carried out generally in good yield, but with a disappointing amount of the diphosphinated species (Table 9). This is surprising, as steric hindrance from the first triphenylphosphine ligand should reduce the ability of another such ligand to approach the metal core.

Product	Yield (%)	By-product	Yield (%)	s/m (%)
 249	60	 250	20	15
 251	58	 252	23	10
 253	28	 254	10	55
 255	59	 256	10	27

(Table 9 – phosphination of cobalt hexacarbonyl complexes)

When 1,3-dipolar cycloaddition was attempted on the triphenylphosphine system we were met with mixed results. On reacting benzonitrile oxide with dicobalt pentacarbonyl triphenylphosphine-2-methylbut-1-en-3-yne **249** only a 15% yield was achieved in a 1:1 mixture of inseparable diastereoisomers. Cycloaddition using benzonitrile oxide and dicobalt pentacarbonyl triphenylphosphine-methyl-(*E*)-hex-2-en-4-ynoate **251** yielded a slightly better result, affording 20% of the target complex **255** with a 3:1 ratio of inseparable diastereoisomers (Table 10). The diastereomeric ratios were estimated using  $^1\text{H}$  NMR spectroscopy. These results were interesting as there was a higher yield with the enyne ester **251**, which is opposite to the observation when using the heterobimetallic system. As a 3:1 d.r. was achieved, this shows how the sterically more encumbered

desymmetrised system had a stereoselective effect on dipolar attack. A major drawback with the triphenylphosphine system, compared with the heterobimetallic system is that the diastereoisomers were not separable, although a diastereomeric ratio was achieved which shows there may be potential in the diastereoselective capability of these systems. No further work was undertaken at this point.

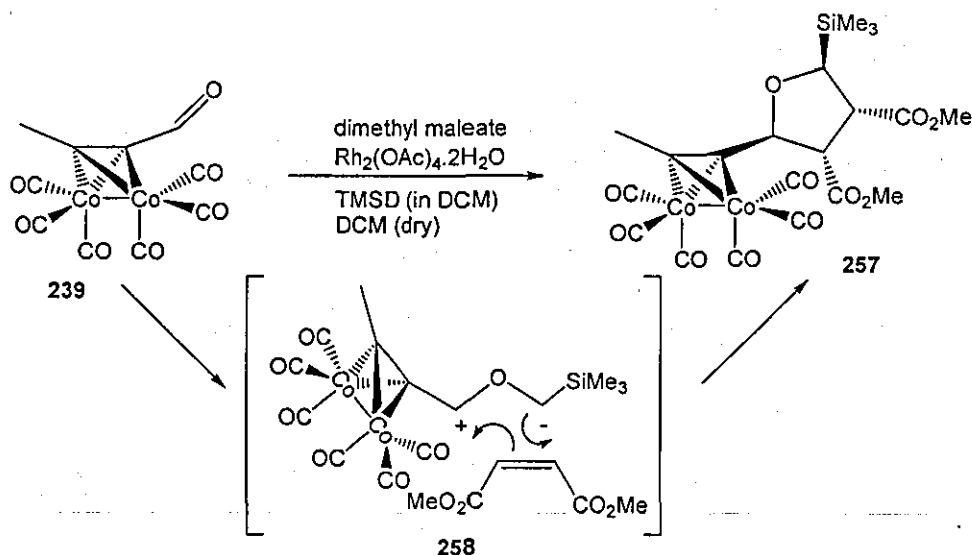
Product	Yield (%)	d.r.	s/m (%)
 253	15	1 : 1	40
 255	20	3 : 1	37

(Table 10 - 1,3-dipolar cycloaddition of desymmetrised triphenylphosphine enyne complexes)

#### 2.4.5 Synthesis of furan derivatives using carbonyl ylids

A report in the literature disclosing a catalytic, three component synthesis of diastereomerically enriched tetrahydro- and dihydrofuran derivatives using homobimetallic cobalt systems *via* a novel 1,3-dipolar carbonyl ylid mechanism, prompted us to investigate what effect using the heterobimetallic system would have under these conditions.<sup>104</sup> In this work the dipole rather than the dipolarophile is attached to the bimetallic alkyne complex. Our primary task was to repeat one of Jamison's examples and check we could create comparable results. Taking dicobalt hexacarbonyl-butynal **239** in a pre-dried flask containing dimethyl maleate and catalytic dirhodium tetraacetate dihydrate dimer  $\text{Rh}_2(\text{OAc})_4 \cdot 2\text{H}_2\text{O}$  in dry DCM under an atmosphere of nitrogen gas, was added

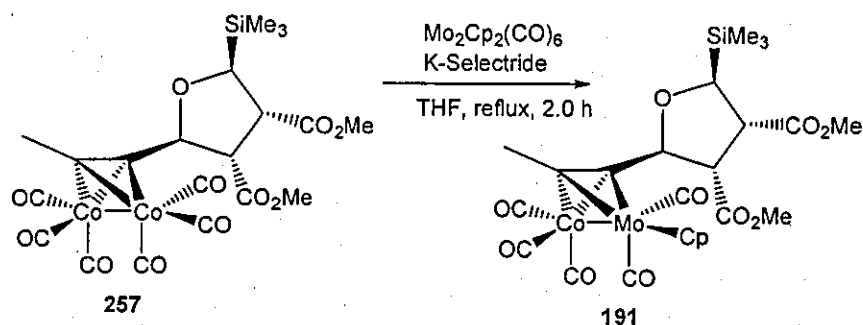
dropwise (trimethylsilyl)diazomethane (TMSD) in DCM over 6.0 h at ambient temperature (Scheme 85). The desired *cis*-product **257** was isolated and purified in 44% yield (lit., 74%, > 20:1 d.r.), therefore we used the same procedure on the heterobimetallic aldehyde system.



(Scheme 85 – synthesis of a homobimetallic furan derivative)

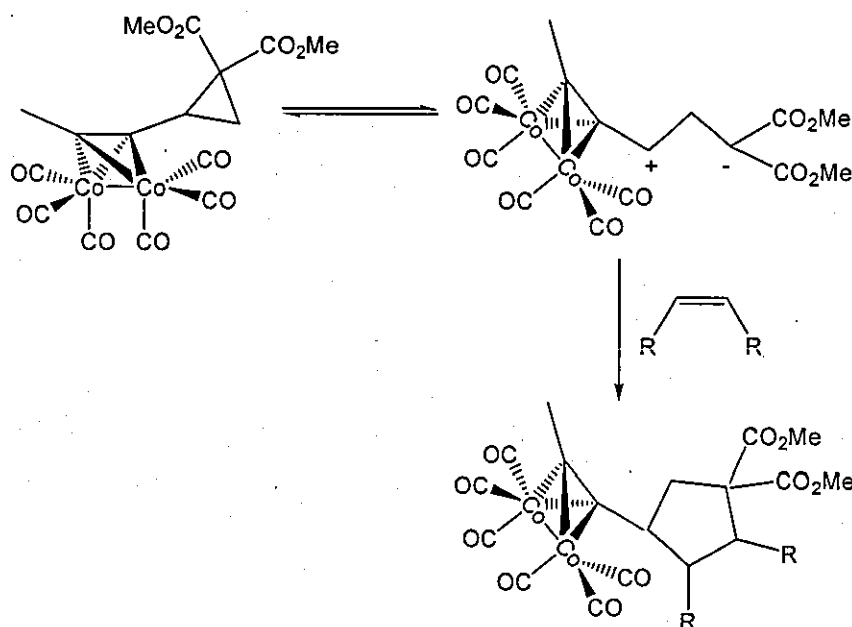
Reaction at 25°C showed no sign of product, with up to 70% of the aldehyde being recovered; therefore it is unlikely the carbonyl ylide is being created at this temperature. When the temperature was increased to reflux in DCM, disappearance of the aldehyde was evident, therefore presumably formation of the carbonyl ylide was occurring. Isolation of the desired product was difficult due to low yields (approximately 10-15%), co-elution with unreacted dimethyl maleate and an unidentified by-product, but it is unknown where the remainder of the complex is lost. To try and confirm synthesis using the heterobimetallic system, the homobimetallic furan **257** was subjected to isolobal displacement with molybdenum cyclopentadiene tricarbonyl dimer and K-Selectride. After refluxing in dry THF for 2.0 h, the corresponding product **191** was isolated as a 1.3:1 mixture of separable diastereoisomers in a 51% combined yield (Scheme 86). Direct comparison with the synthesised heterobimetallic furan confirmed the first eluting diastereoisomer was being fashioned under the carbonyl ylide conditions.





(Scheme 86 – isolobal displacement to form a heterobimetallic furan derivative)

After the disappointing results with the carbonyl ylid cycloadditions we determined to look for an alternative system with a 1,3-dipole function attached to the alkyne complex. Recognising the stability of the Nicholas-type propargyl cation, we planned to combine this with a stabilised anionic centre. Thus we propose the activated cyclopropane system (Scheme 87) which under appropriate conditions should open to behave as a 3-carbon 1,3-dipole for trapping by, for example, alkenes to form cyclopentanes. Furthermore, Nicholas cation formation by carbon-carbon bond cleavage has not been reported to date, as far as we are aware. Our studies in this area feature in the subsequent sections.



(Scheme 87 – trapping of 1,3-dipoles with alkenes)

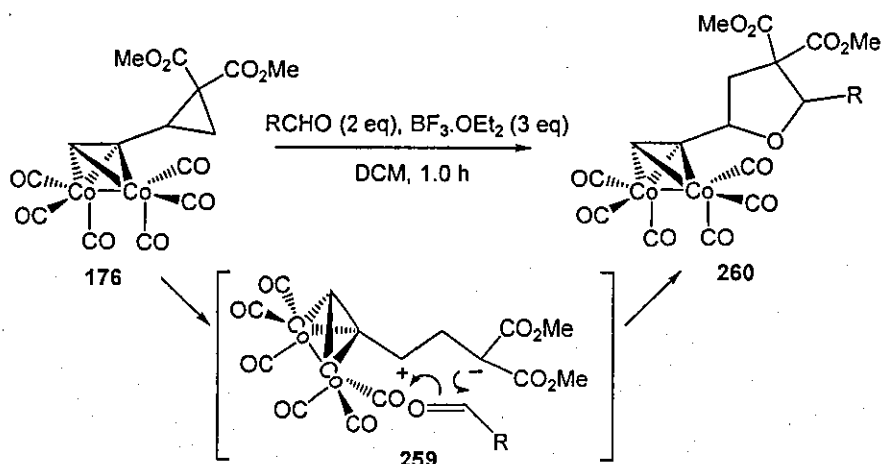
## 2.5 Novel trapping of Nicholas stabilised ring opened cyclopropanes

### 2.5.1 Background

The use of Nicholas methodology is a well established method of incorporating nucleophiles at propargylium cationic centres,<sup>4</sup> with its application to the synthesis of ether ring systems being a popular step in routes to natural products.<sup>105-109</sup> Palladium catalysed ring opening of alkylidene-cyclopropanes and subsequent cyclisation with double bond species to form five-membered ring systems has previously been reported by Tsuji,<sup>110</sup> Yamamoto<sup>111-113</sup> and Trost.<sup>114</sup> This, along with an account of a three component assembly of oxygen heterocycles using a homobimetallic carbonyl ylid complex and trapping with olefins by Jamison,<sup>104</sup> led us to combine these methodologies to create a novel route to highly functionalised five-membered ring species. The basis of this route is an activated cyclopropane carrying cation stabilising (bimetallic alkyne complexed) and anion stabilising (diester) substituents.

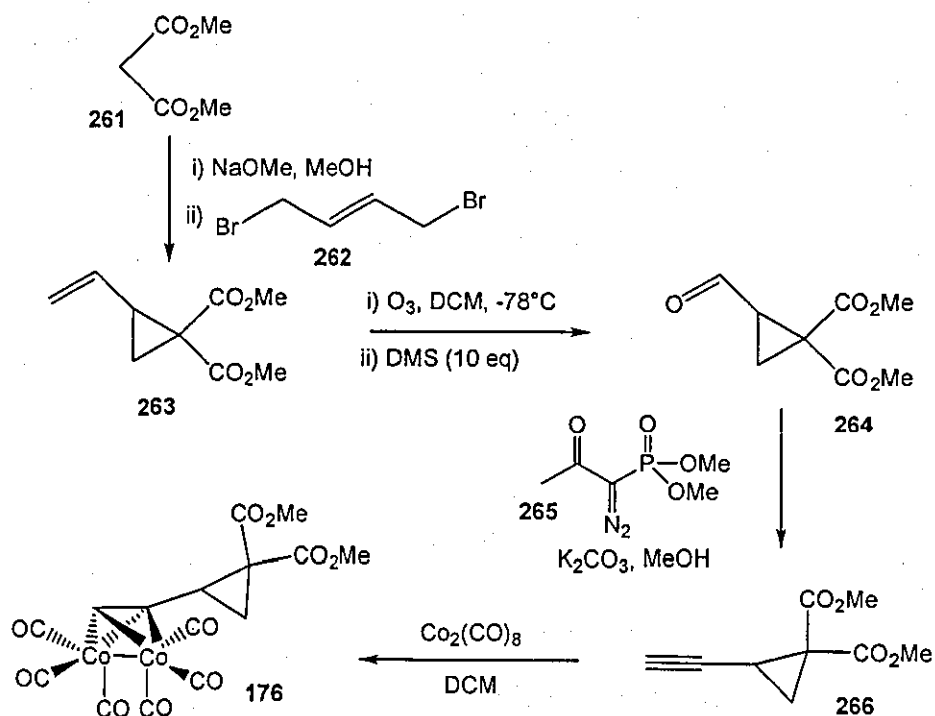
### 2.5.2 Development of the homobimetallic cyclopropane

Dicobalt hexacarbonyl-2-ethynylcyclopropane-1,1-dicarboxylic acid dimethyl ester **176** was synthesised. It was suggested that on treatment with boron trifluoride etherate this would form a doubly stabilised 1,3-dipole **259** which could be trapped with a wide range of aldehydes and imines to form highly functionalised tetrahydrofuran **260** and pyrrolidine molecules (**Scheme 88**). Ring opening of the highly strained cyclopropane *via* cleavage of a carbon-carbon bond, generates a Nicholas carbocation at the propargylic centre and a doubly stabilised anion adjacent to the diester.



(Scheme 88 - assembly of highly functionalised tetrahydrofuran molecules *via* a novel 1,3-dipole)

Synthesis of dicobalt hexacarbonyl-2-ethynylcyclopropane-1,1-dicarboxylic acid dimethyl ester 176 (homobimetallic cyclopropane) was achieved in a four step methodology (Scheme 89).



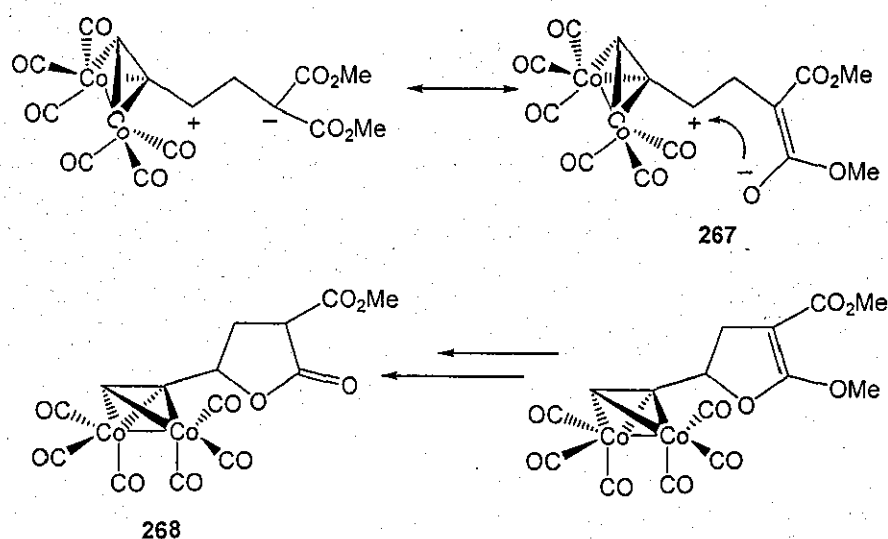
(Scheme 89 - synthesis of complexed homobimetallic cyclopropane)

Initially 2-ethenylcyclopropane-1,1-dicarboxylic acid dimethyl ester **263** (vinyl cyclopropane) was created by deprotonation of dimethyl malonate **261** with sodium methoxide and subsequent addition of *trans*-1,4-dibromobutene **262** to give the vinyl cyclopropane as a colourless oil in 90% yield. The alkene was then oxidized to the aldehyde *via* ozonolysis, isolating 2-formylcyclopropane-1,1-dicarboxylic acid dimethyl ester **264** in 91% yield after breaking down the ozonide with dimethylsulfide and extracting the residual dimethylsulfoxide on washing with water. The crude product was consequently reacted with dimethyl 1-diazo-2-oxopropylphosphonate **265** (Bestmann reagent)<sup>115</sup> and K<sub>2</sub>CO<sub>3</sub> in methanol to generate 2-ethynylcyclopropane-1,1-dicarboxylic acid dimethyl ester **266** (alkyne cyclopropane) in a variable 20-60% yield after purification. No increase in yield was seen on purification of the aldehyde. The Bestmann reagent was fashioned in 95% yield on reacting tosyl azide with dimethyl 2-oxopropylphosphonate in a mixture of benzene and THF. Finally the alkyne cyclopropane was complexed with cobalt octacarbonyl in DCM to form the corresponding starting material, in high yield (90%). When the alkyne cyclopropane was not subjected to column chromatography, only extracting the crude product into diethyl ether and then complexing with cobalt octacarbonyl in DCM, a more reproducible 35-45% overall yield was established.

### 2.5.3 Optimisation studies

Preliminary trials with dimethyl maleate and a range of solvents and Lewis acids were disappointing, recovering starting material in various quantities with TiCl<sub>4</sub>, HBF<sub>4</sub>, SnCl<sub>4</sub> and ZnBr<sub>2</sub> in DCM, THF and MeCN, the harsher Lewis acids decomplexing more of the metal complex. A more polar spot was evident by TLC with both AlCl<sub>3</sub> and BF<sub>3</sub>.OEt<sub>2</sub> in DCM, which on scale up yielded an intramolecularly cyclised product in 55% with BF<sub>3</sub>.OEt<sub>2</sub> (Scheme 90). AlCl<sub>3</sub> was less effective, yielding only 15%. On opening of the cyclopropane, it is postulated that the stabilised negative charge ring closes *via* the alternative oxygen site and the activated enol ether **267** is hydrolysed on workup to afford the lactone **268**. Although it was disappointing that intermolecular reaction with the alkene had not occurred, the cyclopropane was ring opening therefore trapping with further

nucleophiles could be attempted. The lactone also has an acidic proton between the two carbonyl groups, which on treatment of base and then an electrophile would create a quaternary centre, but due to time restraints this has not been explored.

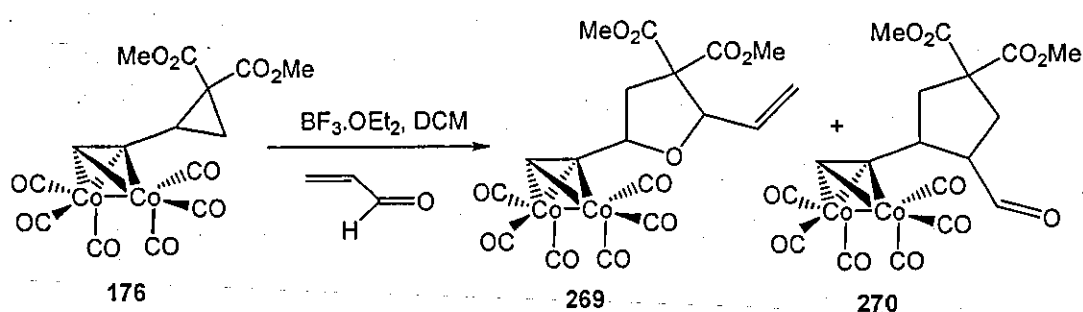


(Scheme 90 - intramolecularly trapped dicobalt hexacarbonyl-(3-methoxycarbonyltetrahydrofuran-2-on-5-yl)-ethyne by-product)

Further reactions with dimethyl maleate and ethyl acrylate with  $\text{BF}_3 \cdot \text{OEt}_2$  only yielded the intramolecularly cyclised product and no intermolecular cycloaddition product was evident, even under reflux for 3.0 h. With this result in mind we decided to try a more reactive electrophile, so we turned our attention to reaction with propenal which gave the prospect of reacting either *via* the alkene or aldehyde  $\pi$ -bond fragments of the molecule. The lactone product is also a common by-product in all medium to low yielding reactions, as this ring expansion competes with intermolecular cyclisation.

In our initial studies, we found that using one equivalent of propenal and  $\text{BF}_3 \cdot \text{OEt}_2$  in DCM, afforded only 5% each of the desired tetrahydrofuran **269** in 1:1 d.r and cyclopentane **270** product in 2:1 d.r, alongside 40% of the intramolecularly trapped dicobalt hexacarbonyl-(3-methoxycarbonyltetrahydrofuran-2-on-5-yl)-ethyne **268**, all three of which were separable by standard column chromatography. On increasing the quantities

to two equivalents of propenal and three equivalents of  $\text{BF}_3 \cdot \text{OEt}_2$ , optimal yields of 24 and 21% were achieved in identical diastereoselectivity to before (**Scheme 91**). Increasing the equivalents of propenal further only made purification more difficult and increased equivalents of Lewis acid only further decomplexed the homobimetallic species. All reactions had to be carried out in dry conditions, under an atmosphere of nitrogen. When the DCM or reaction vessel was not dried, generally no reaction occurred and only the starting material was isolated. If the reaction was carried out in air, the reaction mixture slowly decomposed, therefore reducing yields.

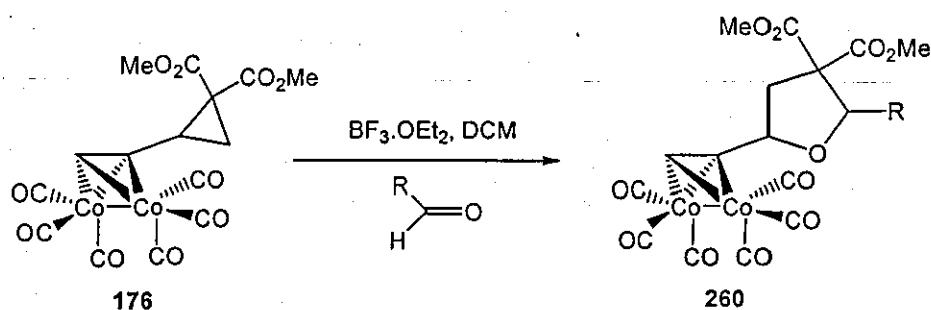


(Scheme 91 - cyclisation of complexed cyclopropane with propenal)

Remarkably, both the alkene and aldehyde units reacted in almost equal quantities, in formation of the furan **269** and cyclopentane **270** ring systems respectively. No diastereoselection was evident on reaction with the aldehyde, but interestingly a 2:1 d.r. was identified by  $^1\text{H}$  NMR for the cyclopentane, signifying a preference of attack most likely by reducing steric interactions with the metal complex. Following a positive result with propenal and disappointing results with the limited range of alkenes attempted, we decided to proceed further with aldehyde substrates. These are the first examples, to our knowledge, of Nicholas cation generation by carbon-carbon bond cleavage rather than carbon-heteroatom cleavage.

### 2.5.4 Cyclisation with aldehydes

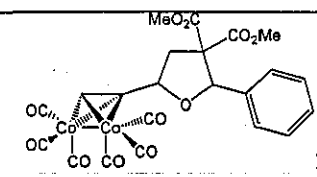
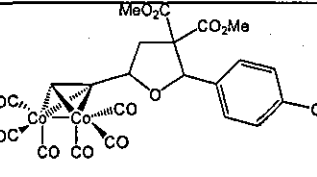
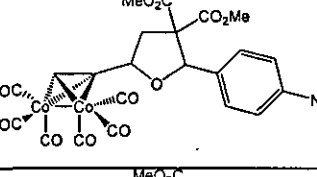
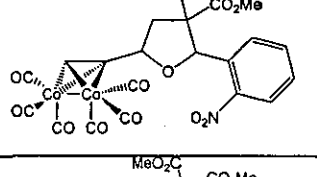
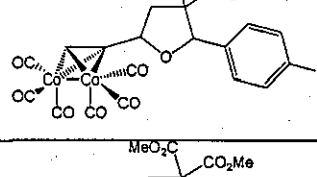
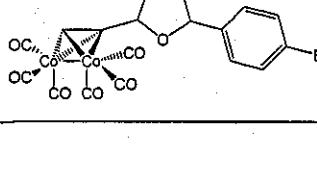
During our primary investigations with aldehyde substrates, we found that using one equivalent of benzaldehyde and  $\text{BF}_3 \cdot \text{OEt}_2$  afforded the desired tetrahydrofuran product **260** in 1:1 d.r, but in only 10% yield along with up to 40% of the intramolecularly trapped dicobalt hexacarbonyl-5-ethynyl-2-oxo-tetrahydrofuran-3-carboxylic acid methyl ester **268**. On increasing to two equivalents of aldehyde and three equivalents of  $\text{BF}_3 \cdot \text{OEt}_2$ , in DCM yields were first optimised at  $0^\circ\text{C}$ , because in previous experiments at higher temperatures decomplexation by the Lewis acid had been a problem. On performing reactions at reflux, however, generally higher yields and sometimes higher diastereomeric ratios were attained (Scheme 92). Increasing the equivalents further, only made purification and decomplexation more of a problem.



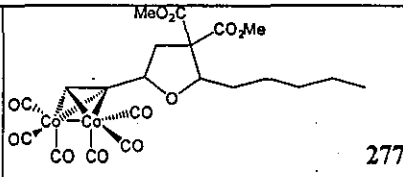
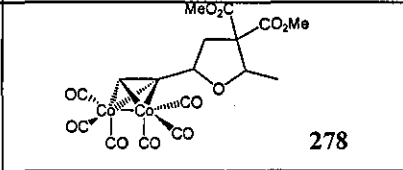
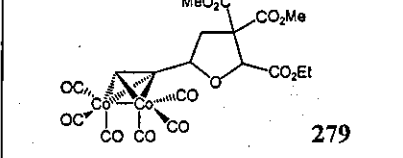
(Scheme 92 - cyclisation of complexed cyclopropane with aldehydes)

Experiments with a series of aldehydes showed that good to excellent yields were attained with alkyl aldehydes, electron-deficient aromatic aldehydes and ethyl glyoxylate. Yields were reduced or nil with electron-rich aromatic aldehydes and on increasing steric hindrance (Table 11). This is consistent with the varied activities of the aldehydes, as no cyclisation was achieved with anisaldehyde, which would have the least activated carbonyl group, due to the electron donating properties of the methoxy substituent. No diastereoselectivity was achieved with the majority of 4-aryl or *n*-alkyl groups, except on reaction with 4-fluorobenzaldehyde, when at ambient temperature or reflux a d.r. of 1.7:1 was achieved in a ratio of *trans*- to *cis*-isomers; this was repeated to confirm. It is not

known why this is an exception and it is made more unusual as no diastereoselectivity was achieved at 0°C. Reacting the homobimetallic complex with ethyl glyoxylate also provided a d.r, but this time the *trans*-isomer was in excess (1.6:1). A further trial with 2-nitrobenzaldehyde was carried out to see if steric hindrance had any effect on d.r. or yield. Although a 2:1 d.r. in preference of the *trans* isomer was accomplished, the isolated yield was reduced to only 30% at reflux, a drop of 47% in comparison with 4-nitrobenzaldehyde. It seems that on increasing the steric hindrance of the substrate an improvement in diastereoselectivity can be achieved at the expense of a decrease in yield (Table 11).

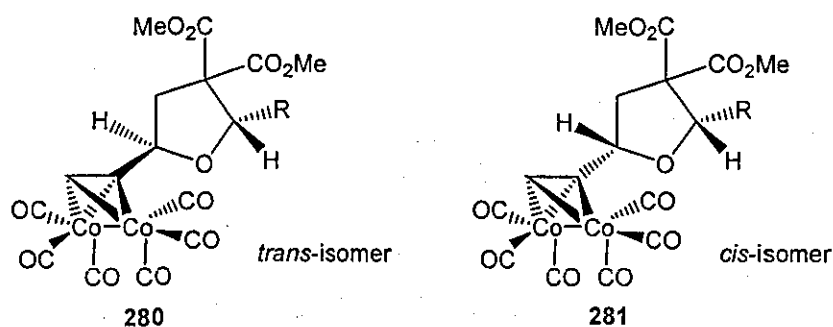
Electrophile	Product	T (°C)	Yield (%)	<i>Trans</i> : <i>Cis</i>
Benzaldehyde	 271	0	60	1 : 1
		25	68	1 : 1
		40	83	1 : 1
Anisaldehyde	 272	0	0	n/a
		25	0	n/a
		40	0	n/a
4-Nitrobenzaldehyde	 273	0	65	1 : 1
		25	72	1 : 1
		40	77	1 : 1
2-Nitrobenzaldehyde	 274	25	23	2 : 1
		40	30	2 : 1
4-Fluorobenzaldehyde	 275	0	85	1 : 1
		25	80	1.7 : 1
		40	81	1.7 : 1
4-Bromobenzaldehyde	 276	0	50	1 : 1
		25	61	1 : 1
		40	67	1 : 1



Hexanal	 277	0	83	1 : 1
		25	72	1 : 1
		40	83	1 : 1
Acetaldehyde	 278	0	74	1 : 1
		25	85	1 : 1
		40	82	1 : 1
Ethyl glyoxylate	 279	25	82	1.4 : 1
		40	86	1.6 : 1

(Table 11 - Lewis acid mediated ring opening of homobimetallic cyclopropane and intermolecular trapping with aldehydes)

The relative stereochemistry between C-2 and C-5 of the tetrahydrofuran can be assigned from the shifts of the CH<sub>2</sub> protons in the ring with the *cis* or *trans* arrangement of the adjacent proton. (Scheme 93). A large difference of between 0.60 and 1.09 ppm is seen for the double doublets in the *trans*-isomer 280 and a much smaller 0.09-0.38 ppm difference for the *cis* equivalent 281.



(Scheme 93 - <sup>1</sup>H NMR assignment of the *cis*- and *trans*-isomers)

Confirmation of this prediction was performed by individual nOe difference experiments irradiating H<sub>a</sub> and H<sub>b</sub> for the two separable *cis*- and *trans*-isomers of the 4-



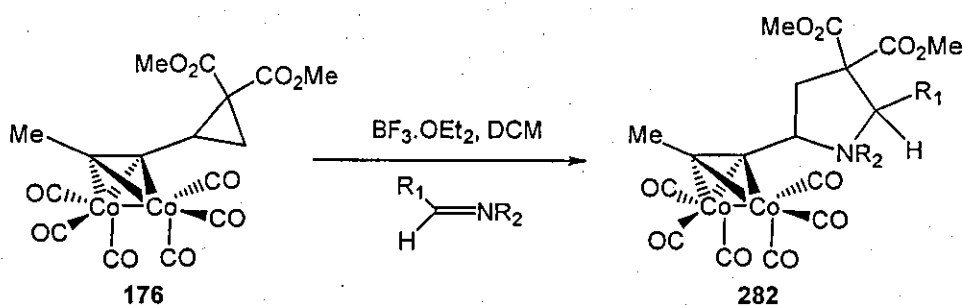
To inspect whether the mixtures of products obtained in these reactions represent the thermodynamically controlled ratios, both of the two separated diastereoisomers of dicobalt hexacarbonyl-5-ethynyl-2-(4-nitrophenyl)tetrahydrofuran-3,3-dicarboxylic acid dimethyl ester **273** were treated individually with  $\text{BF}_3 \cdot \text{OEt}_2$  in DCM at ambient temperature. From both reactions a 1:1 d.r. was obtained, verifying that the thermodynamic mixture of products is being fashioned. This result also established that the carbon-oxygen bond is labile under Lewis acid conditions and this is occurring during the course of the reaction. Therefore two further experiments could be carried out to explore this presumption further. Firstly (2,4-Dimethoxyphenylimino)acetic acid ethyl ester under identical conditions was added to a 1:1 mixture of dicobalt hexacarbonyl-(4-nitrophenyl)tetrahydrofuran-3,3-dicarboxylic acid dimethyl ester **273**, to see whether the carbon-carbon bond is also labile under these conditions and if a mixture of the products of the two electrophiles is isolated. Only a 1:1 mixture of the nitrophenyl compound was attained, showing that when the carbon-carbon bond is created, it cannot be broken under the conditions used and is therefore most likely to be formed in the first step of the mechanism. In an effort to isolate a kinetic ratio of products, a reaction to create the nitrophenyl-furan was followed by TLC after 1, 5, 10 and 15 minutes. After 1, 5 and 10 minutes some homobimetallic cyclopropane was still present, but after 15 min the reaction was complete, but again a 1:1 d.r. was created, therefore either the epimerisation is extremely fast, or there is no diastereomeric preference to which face of the molecule the electrophile approaches.

Finally, as cyclisation with ethyl glyoxylate at reflux provided a 1.6:1 d.r. (*trans:cis*) and it is supplied as a 50% solution in toluene, we thought it might be worth attempting some cyclisations in toluene and chloroform, as these solvents were not initially trialled. Upon reaction of dicobalt hexacarbonyl-2-ethynylcyclopropane-1,1-dicarboxylic acid dimethyl ester **176** with 4-nitrobenzaldehyde and  $\text{BF}_3 \cdot \text{OEt}_2$  at ambient temperature and  $60^\circ\text{C}$ , the desired products were isolated but in reduced yields. Reactions in chloroform created the nitrofuran **273** in 36 and 42% yield with a 1:1 d.r., whereas on using toluene the required compounds were fashioned in 30 and 40% yield, but an increased 2:1 d.r. was achieved with again in preference of the *trans*-isomer, an improvement in diastereoselectivity

compared to reaction in DCM. Unfortunately due to time restraints further reactions in toluene have not been investigated.

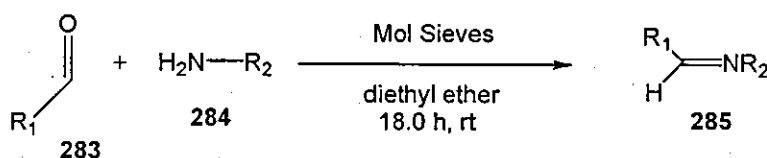
### 2.5.5 Cyclisation with imines

After successful cyclisation with aldehydes to create tetrahydrofurans we decided to attempt similar reactions with a series of imines to form pyrrolidines (**Scheme 94**).



(Scheme 94 - cyclisation of complexed cyclopropane with imines)

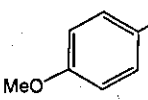
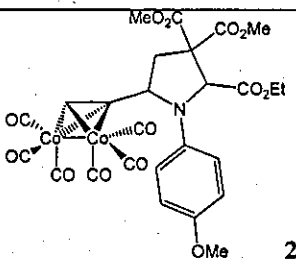
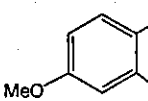
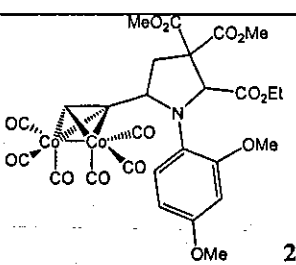
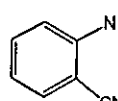
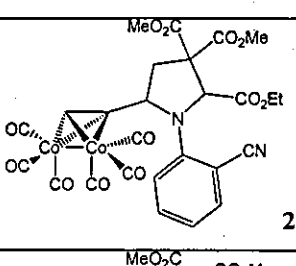
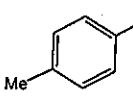
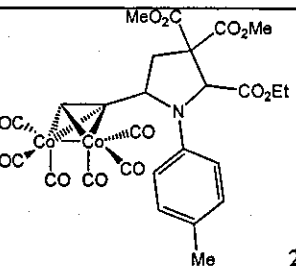
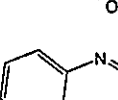
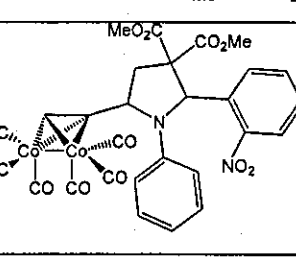
The necessary imines **285** were made upon reaction of the required aldehyde **283** and amine **284** in equimolar quantities, stirring in diethyl ether for 18.0 h over molecular sieves. The desired products were isolated in approximately 95% yield after filtration and concentration *in vacuo* (**Scheme 95**).



(Scheme 95 - synthesis of imine starting substrates)

Using identical conditions as with the aldehyde substrates, generally excellent yields were achieved when there was an electron donating substituent on the nitrogen and an electron withdrawing substituent on the imine carbon. When altering the electronics of the

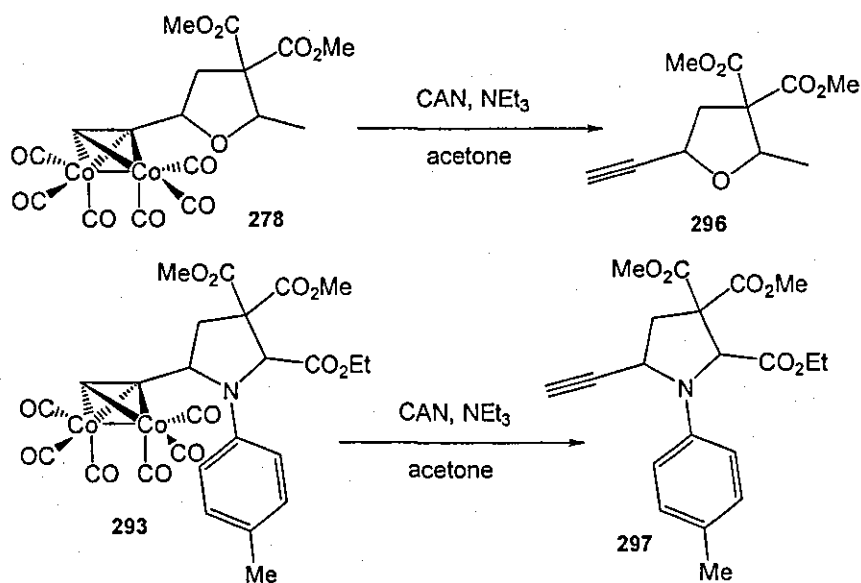
substituents, yields were reduced. On increasing steric hindrance in the *ortho* position on *N*-aromatic imines, diastereoselectivity was achieved, affording a 3:1 d.r. with the 2-cyano derivative **291** in a moderate 52% yield (Table 12).

Electrophile	Product	T (°C)	Yield (%)	<i>Trans</i> : <i>Cis</i>
 <b>286</b>	 <b>287</b>	0 25 40	91 75 91	1 : 1 1 : 1 1 : 1
 <b>288</b>	 <b>289</b>	0 25 40	85 73 80	2 : 1 2 : 1 2 : 1
 <b>290</b>	 <b>291</b>	0 25 40	65 72 69	1 : 2 1 : 3 1 : 3
 <b>292</b>	 <b>293</b>	0 25 40	79 81 85	1 : 1 1 : 1 1 : 1
 <b>294</b>	 <b>295</b>	25 40	23 30	2 : 1 2 : 1

(Table 12 - Lewis acid mediated ring opening of homobimetallic cyclopropane and intermolecular trapping with imines)

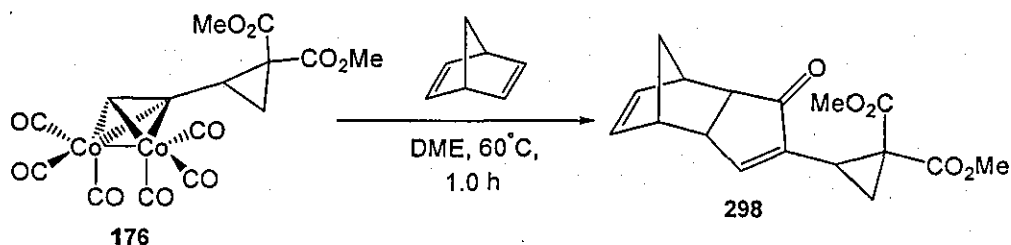
Reaction with (2-nitrobenzylidene)phenylamine **294** provided a 30% yield and 2:1 d.r. of the pyrrolidine product **295**, a decrease in yield compared with the other examples. This is most likely due to the increase in steric hindrance provided by the 2-nitrophenyl substituent.

In an attempt to separate the mixed diastereoisomers of an inseparable homobimetallic furan and pyrrolidine, the metal complex was oxidised using ceric ammonium nitrate and triethylamine in acetone with both dicobalt hexacarbonyl-5-ethynyl-2-methyltetrahydrofuran-3,3-dicarboxylic acid dimethyl ester **278** and dicobalt hexacarbonyl-5-ethynyl-1-(4-methylphenyl)pyrrolidine-2,3,3-tricarboxylic acid 2-ethyl ester 3,3-dimethyl ester **293** (Scheme 96). The expected products were separated and isolated in a 1:1 ratio as yellow oils. 5-Ethynyl-2-methyltetrahydrofuran-3,3-dicarboxylic acid dimethyl ester **296** was generated in a combined 85% yield and 5-ethynyl-1-(4-methylphenyl)-pyrrolidine-2,3,3-tricarboxylic acid 2-ethyl ester 3,3-dimethyl ester **297** in 60%.



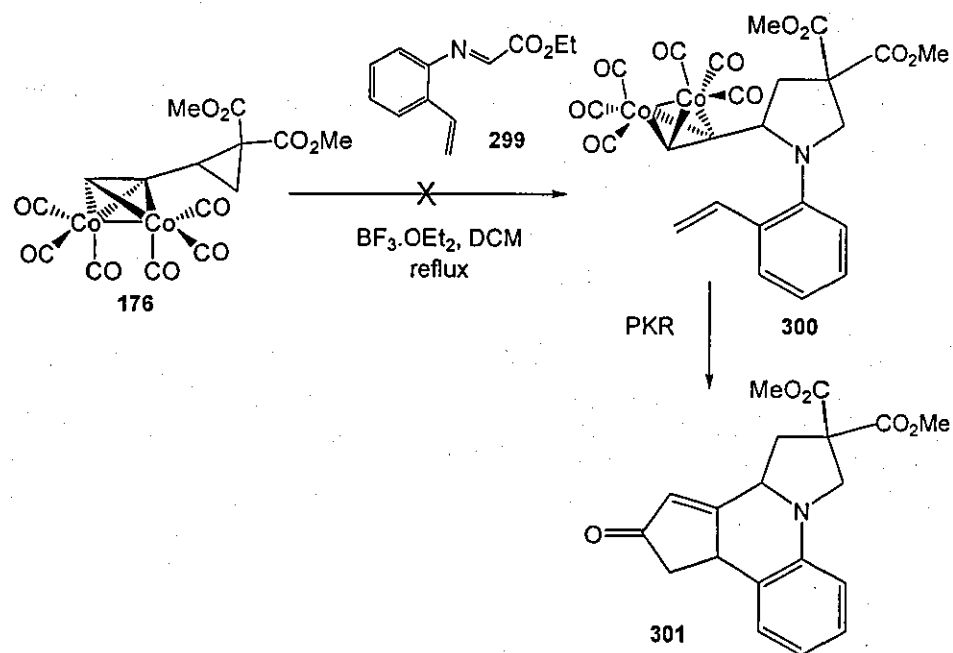
(Scheme 96 - decomplexation of homobimetallic methyl furan)

We were also interested to see whether a Pauson-Khand reaction could be performed on the homobimetallic cyclopropane. Therefore dicobalt hexacarbonyl-2-ethynylcyclopropane-1,1-dicarboxylic acid dimethyl ester **176** was dissolved in dimethoxyethane and norbornadiene added, heating at 60°C for 1.0 h. The expected cyclopentanone **298** was isolated in 60% yield and as a 1.5:1 mixture of diastereoisomers (Scheme 97).



(Scheme 97 - a Pauson-Khand reaction with homobimetallic cyclopropane)

We also wanted to apply the Pauson-Khand reaction to create a tetracyclic molecule **301** in two steps from the homobimetallic cyclopropane **176** (Scheme 98). The required imine **299** was created in 90% yield from 2-ethenylaniline and ethyl glyoxylate, but even after several attempts it would not cyclise *via* the ring opened cyclopropane and only the lactone product **268** was isolated in each case.

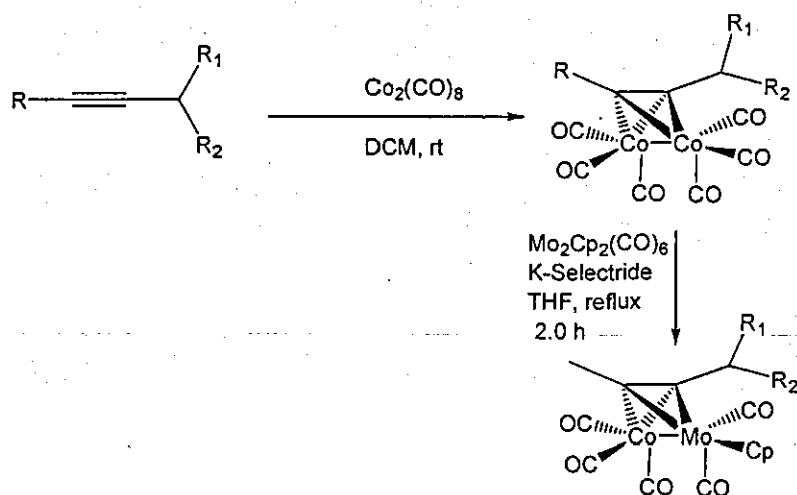


(Scheme 98 - attempted synthesis of a four ring structure in two steps)



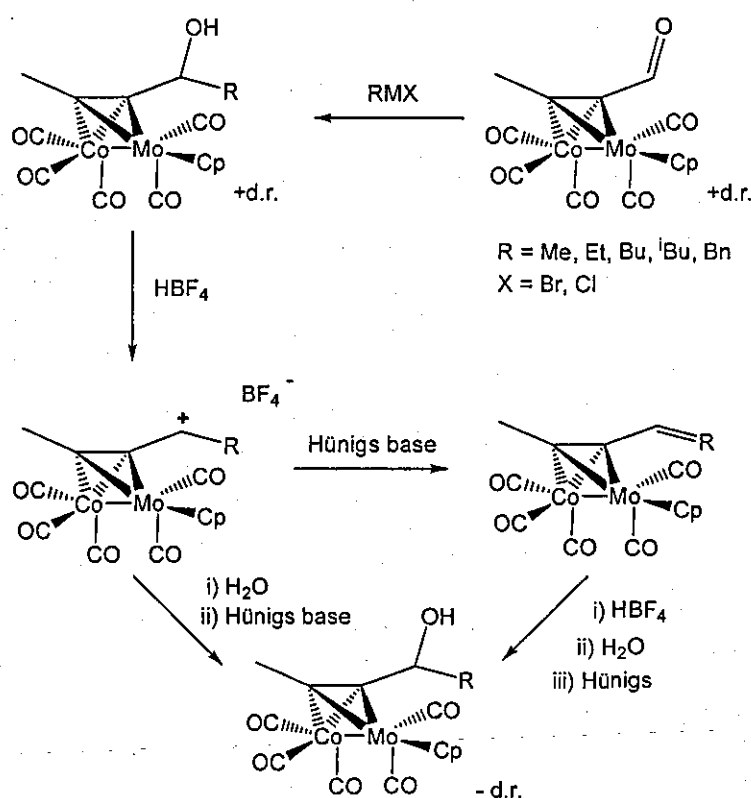
## 2.6 Conclusion

It has been shown that heterobimetallic Co/Mo complexes can be created generally in few steps and high yield, from the starting alkyne substrates. Subsequent isolobal displacement with a molybdenum nucleophile is carried out after complexation with cobalt octacarbonyl and potential modification of the complex. Improvement of yield on utilising K- over L-Selectride also enabled more efficient reactions to occur (Scheme 99).



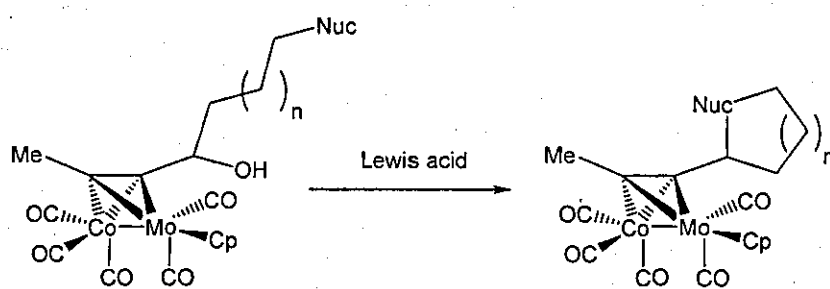
(Scheme 99 - synthesis of heterobimetallic propargylium complexes)

Nucleophilic addition to the aldehyde complex **186** afforded alcohol products **194-198**. Synthesis of heterobimetallic propargylic salt **201-205** (81-93%) and enyne **207**, **211-214** (83-94%) complexes and nucleophilic addition to these, provided the equivalent alcohol products **194-198** in good to excellent yield and moderate to very good d.r. and in reverse d.r. to the equivalent Grignard addition products (Scheme 100). Oxygen, sulfur and nitrogen nucleophiles could be used, but to date carbon nucleophiles still pose a problem.



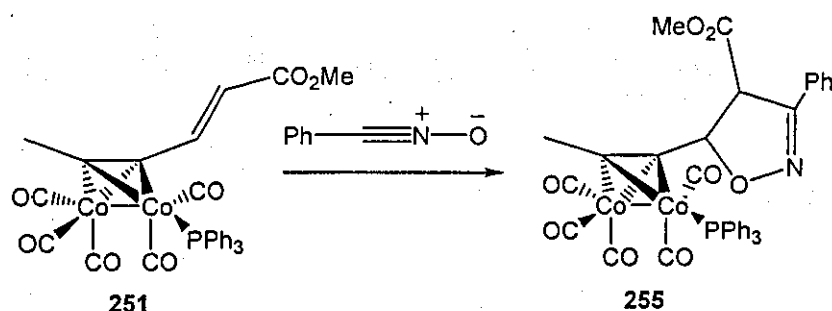
(Scheme 100 – nucleophilic addition to enyne and salt complexes)

Intramolecular nucleophilic addition to a Nicholas cation to create oxygen heterocycles was achieved, in poor to very good yield but unfortunately reduced d.r. on comparison with intermolecular nucleophilic addition. An extensive investigation was not carried out and there is potential for optimisation of these systems using more hindered substrate examples and further nucleophilic species (Scheme 101).



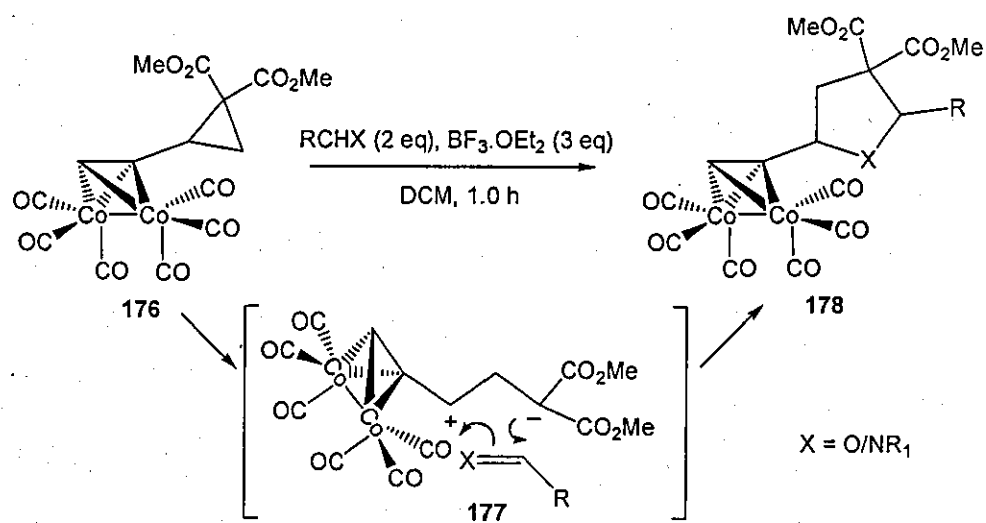
(Scheme 101 - intramolecular nucleophilic addition)

Employing the previously created enyne complexes, 1,3-dipolar cycloadditions were undertaken with benzonitrile oxide to form isoxazolines. Treatment with the less electron-rich homobimetallic enynes **240** and **243** worked well, but on the use of heterobimetallic and desymmetrised triphenylphosphine enyne complexes **187**, **188**, **213**, **213**, **249** and **251**, yields were reduced and diastereoselectivity (3:1 d.r.) was only established with one example (Scheme 102).



(Scheme 102 - 1,3-dipolar cycloaddition with enynes)

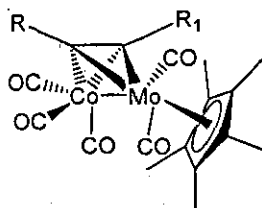
Highly substituted tetrahydrofuran **271-279** and pyrrolidine **287**, **289**, **291**, **293**, **295** species were synthesised in good to excellent yield *via* a novel 1,3-dipolar cyclisation with aldehydes and imines, by means of a Nicholas carbocation and a doubly stabilised negative charge created from ring opening of a homobimetallic cyclopropane **176** (Scheme 103). Although diastereoselectivity was moderate at best, it should improve on extension to desymmetrised systems. Optimal yields were achieved for electronically favourable and sterically less hindered substrates. Diastereoselectivity improved for more hindered systems, but generally at the expense of yield.



(Scheme 103 - trapping of homobimetallic cyclopropanes with electrophiles)

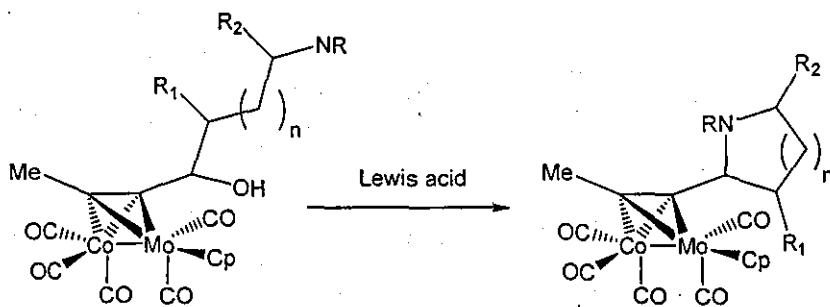
## 2.7 Future Plans

It has been demonstrated how the cobalt-molybdenum heterobimetallic core encourages diastereoselectivity in nucleophilic attack to propargyl aldehyde, alkene and Nicholas salt complexes. Improvement in diastereoselectivity could be achieved by replacing the Cp ligand on the molybdenum centre by a bulkier pentamethylcyclopentadienyl (Cp\*) ligand (Scheme 104). This will enhance the steric differentiation between the cobalt and molybdenum centre, thus approach of a nucleophile should be more favourable *via* the cobalt face of the molecule.



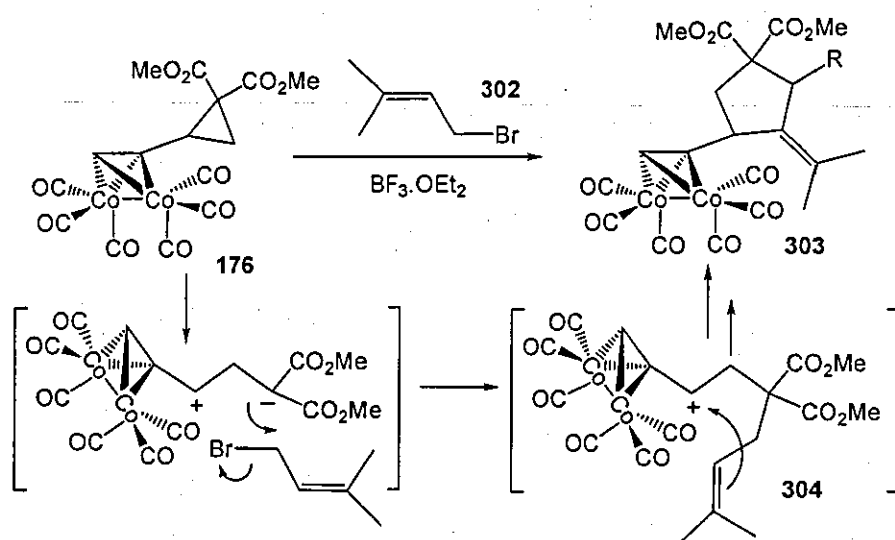
(Scheme 104 – the heterobimetallic complex with a Cp\* ligand)

Intramolecular nucleophile capture was only undertaken with a narrow range of substrates, with limited diastereoselectivity obtained from the small sterically unencumbered systems used. Increasing the size of substituents on the side chain, should encourage attack from the less hindered cobalt face and promote higher diastereoselectivity. Extension to nitrogen nucleophiles, to generate pyrrolidine ring systems is also an area of interest (Scheme 105).



(Scheme 105 - intramolecular nucleophilic addition)

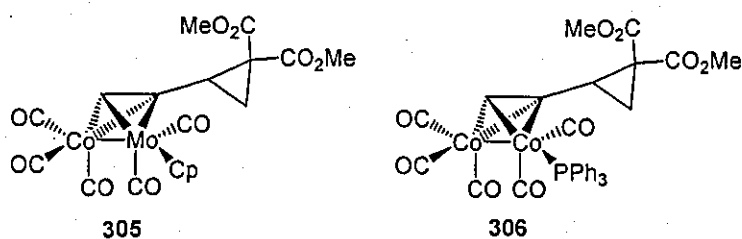
After successful cyclisation of aldehydes and imines with a cyclopropane ring opened 1,3-dipole, extension to activated alkenes, ketones and epoxides is of great interest. In particular, reactions with 3-buten-2-one, cinnamaldehyde and 1-bromo-3-methyl-2-butene **302** pose exciting outcomes. Due to propenal reacting through both the alkene and aldehyde, will but-3-en-2-one also react *via* both the ketone and alkene? The same scenario is present in the alkene and aldehyde of cinnamaldehyde. Another class of substrates including 1-bromo-3-methylbut-2-ene **302**, show potential in creation of cyclopentane ring structures **303**. The negative charge could substitute bromine and the alkene **304** then trap the Nicholas carbocation, to leave a tertiary cation which can be quenched by proton abstraction, with the most substituted alkene product most likely to be formed **303** (Scheme 106).



(Scheme 106 - trapping of homobimetallic cyclopropanes with 1-bromo-3-methylbut-2-ene)

Desymmetrising the metal core with both  $\text{PPh}_3$  and  $\text{MoCp}(\text{CO})_2$  in an attempt to increase the diastereoselectivity of the reaction, is another option to explore. Due to the negative charge being so far away from the metal core, the initial step should not be affected by the electronic change in the metal centre, but the extra stability of the Nicholas cation by molybdenum may favour the cyclopropane ring opening reaction. This could pose a

problem in producing and isolating the cyclopropane **305**, under reflux in THF conditions. An initial reaction to isolate dicobalt triphenylphosphine cyclopropane **306** was accomplished in good yield and 3:1 d.r. Upon reaction with 4-nitrobenzaldehyde the d.r. increased from 1:1 to 3:1 in comparison with the homobimetallic system. Although the yield was reduced, this demonstrated the potential of heterobimetallic and desymmetrised systems in this novel reaction (Scheme 107).



**(Scheme 107 - heterobimetallic and desymmetrised cyclopropane)**

### 3.0 Experimental

#### General information

All reactions herein were carried out in one of the following solvents which were dried and purified, or purchased in the following procedures.

Acetone	Stirred over anhydrous potassium carbonate, followed by distillation over anhydrous calcium sulfate.
Acetonitrile	Purchased from Aldrich (99.8%), Sure/Seal™ anhydrous quality.
Benzene	Purchased from Aldrich (99+%) and used without further purification.
Chloroform	Purchased from Fischer Scientific (99+%), used without purification for general use or distilled over CaH <sub>2</sub> for anhydrous reactions.
Dichloromethane	For general use CH <sub>2</sub> Cl <sub>2</sub> was distilled over boiling stones or CaH <sub>2</sub> for anhydrous reactions.
Diethyl ether	Purchased from Fischer Scientific (99+%), used without purification for general use or distilled over sodium and benzophenone for anhydrous reactions.
Diglyme	Distilled over sodium and benzophenone.
1,2-Dimethoxyethane	Purchased from Lancaster (99+%), degassed by purging under a flow of nitrogen before use.
Dimethylformamide	Purchased from Aldrich, Sure/Seal™ anhydrous quality.
Dimethylsulfide	Purchased from Aldrich (99+%) and used without further purification.
Ethyl acetate	Distilled over CaCl <sub>2</sub> for general use.
<i>n</i> -Hexane	Purchased from Fischer Scientific (99+%), used without purification for general use.
Light petroleum	Distilled over CaCl <sub>2</sub> for general use, collecting the fraction distilling below 60°C.
Tetrahydrofuran	Distilled over sodium and benzophenone.



$\text{Mo(CO)}_6$  was purchased from Fluka and  $\text{Co}_2(\text{CO})_8$  from Strem (stabilised by 1-5% hexane), both used without any further purification.

Anhydrous reactions were extensively flame-dried under an atmosphere of nitrogen.

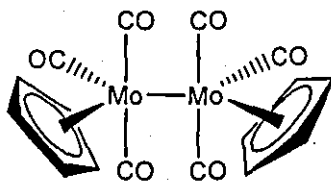
All metal carbonyl complexes were stored under a nitrogen atmosphere and kept at  $-18^\circ\text{C}$  in a freezer.

Analysis of the compounds created herein was made using a number of the following instruments and procedures indicated below.

High resolution mass spectroscopy was carried out on a Jeol SX 102 machine, used for both electron ionisation (EI) and fast atom bombardment (FAB) ionisation techniques. For FAB spectroscopy a matrix of 1,3-nitrobenzylalcohol was used to dissolve the compounds under investigation, prior to ionisation. Nuclear magnetic resonance spectroscopy was acquired using either a Bruker AC 250 or Bruker DPX 400 instrument. The spectra were calibrated where possible to the signals of tetramethylsilane or the small quantity of  $\text{CHCl}_3$  present in  $\text{CDCl}_3$ , typically used as the standard solvent for these experiments. Where possible coupling constants ( $J$ ) are shown denoting their multiplicity as a singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m) or broad signal (br) etc. The size of the coupling constants are given in Hertz (Hz). Elemental analysis was carried out using a Perkin Elmer CHN 2400 elemental analyser. Fourier transform Infra Red spectroscopy was recorded using a Paragon 1000 Perkin Elmer FT-IR spectrometer in the range of  $3500\text{-}600\text{cm}^{-1}$  following a standard background correction. Melting points of solid products was recorded using a Stuart Scientific SMP3 instrument.

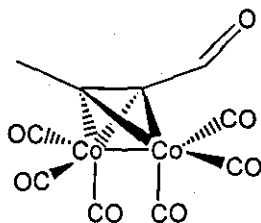
Flash silica column chromatography was used as a standard purification procedure using Fluka Kiesel gel 60, 0.04-0.063 mm particle size silica. Thin layer chromatography was used where possible as a standard procedure for monitoring the course and rate of a given reaction. TLC plates used were Merck aluminium backed sheets with Kiesel gel 60 F<sub>254</sub> silica coating.

**Molybdenum cyclopentadienyl tricarbonyl dimer (183)<sup>116</sup>**



Dicyclopentadiene was cracked at 175°C and the fraction boiling between 35-45°C was collected. The freshly prepared cyclopentadiene (6.00 mL, 70.00 mmol) was then added dropwise at 0°C to a flame-dried three-necked RBF containing a suspension of NaH (1.400 g, 35.00 mmol) in dry diglyme (150 mL) and stirred at ambient temperature for 1.0 h. To the resultant dark pink/purple solution was added molybdenum hexacarbonyl (8.800 g, 25.00 mmol) and *n*-hexane (5 mL). The reaction mixture was then stirred at reflux for 2.0 h. After cooling the orange solution to ambient temperature, methanol (5 mL) was added slowly, followed by distilled water (5 mL). To the reaction mixture was added a pre-filtered solution containing distilled water (250 mL), concentrated acetic acid (15 mL) and hydrated iron (III) sulfate (20.000 g), which led to formation of a dark purple precipitate. This was filtered and washed with distilled water (250 mL), cold methanol (50 mL) and cold *n*-hexane (50 mL). The product was then dried under suction to yield the *title complex* as a dark purple powder (5.920 g, 48%);  $\nu_{\max}$  (nujol)/cm<sup>-1</sup> 2951 (sp<sup>3</sup> C-H), 1950, 1900, 1884 (C≡O);  $\delta_{\text{H}}$  (250 MHz; CDCl<sub>3</sub>) 5.49 (10H, s, CpH);  $\delta_{\text{C}}$  (100 MHz; CDCl<sub>3</sub>) 92.4 (CpC), 229.3, 229.5 (MoCp(CO)<sub>3</sub>).

**Dicobalt hexacarbonyl-2-butyne (239)<sup>117</sup>**

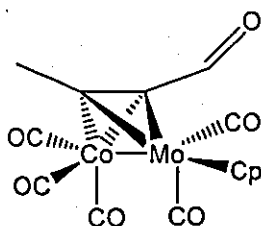


Dicobalt octacarbonyl (1.580 g, 4.57 mmol) was added to DCM (75 mL) under an atmosphere of nitrogen. To this was added 2-butyne diethyl acetal (0.650 g, 4.57 mmol). The reaction mixture was then stirred at room temperature for 1.0 h. Distilled

water (1 drop) was then added with *p*-toluenesulfonic acid (a spatula measure, 0.150 g approx). The reaction mixture was stirred at room temperature for 24.0 h, monitoring by TLC. Additional *p*-toluenesulfonic acid was added, if the reaction did not proceed to greater than 60-70% by TLC. Solid NaHCO<sub>3</sub> (two spatula measures) was then added prior to filtration and concentration *in vacuo*. The crude product was purified by flash silica column chromatography eluting with petroleum ether-diethyl ether (20:1 v/v) to yield the *title complex* as a deep red oil (1.300 g, 80%) (Found: M<sup>+</sup>, 353.8623. C<sub>10</sub>H<sub>4</sub>O<sub>7</sub>Co<sub>2</sub> requires M, 353.8621);  $\nu_{\max}$  (film)/cm<sup>-1</sup> 2907, 2807 (sp<sup>3</sup> C-H), 2101, 2028 (C≡O), 1670 (C=O);  $\delta_{\text{H}}$  (250 MHz; CDCl<sub>3</sub>) 2.74 (3H, s, CH<sub>3</sub>), 10.30 (1H, s, CHO);  $\delta_{\text{C}}$  (100 MHz; CDCl<sub>3</sub>) 21.0 (CH<sub>3</sub>), 87.9 (CCH<sub>3</sub>), 95.3 (CCCH<sub>3</sub>), 191.1 (CHO), 198.4 (Co(CO)<sub>3</sub>); *m/z* 354 (M<sup>+</sup>, 48%), 326 (75), 298 (84), 270 (92).

Dicobalt hexacarbonyl-2-butyne diethyl acetal **193**<sup>117</sup> was also isolated as a deep red oil (0.280 g, 15%) (Found: M<sup>+</sup>, 427.9358. C<sub>14</sub>H<sub>14</sub>O<sub>8</sub>Co<sub>2</sub> requires M, 427.9353);  $\nu_{\max}$  (film)/cm<sup>-1</sup> 2980, 2092 (sp<sup>3</sup> C-H), 2050, 2019 (C≡O), 1104, 1055, 1012 (C-O);  $\delta_{\text{H}}$  (250 MHz; CDCl<sub>3</sub>) 1.22-1.28 (6H, t, *J* 14.1 Hz, CH(OCH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 2.68 (3H, s, CCH<sub>3</sub>), 3.67-3.78 (4H, m, CH(OCH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 5.49 (1H, s, CCH);  $\delta_{\text{C}}$  (100 MHz; CDCl<sub>3</sub>) 15.3 (CH<sub>2</sub>CH<sub>3</sub>), 21.0 (CCH<sub>3</sub>), 63.3 (CH<sub>2</sub>CH<sub>3</sub>), 92.1 (CCCH<sub>3</sub>), 94.3 (CCCH<sub>3</sub>), 102.4 (CH(OCH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 198.5, 199.4, 200.1 (Co(CO)<sub>3</sub>); *m/z* 428 (M<sup>+</sup>, 3%), 400 (30), 383 (36), 372 (100), 355 (40), 344 (80), 327 (17), 316 (55), 288 (54).

### Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-2-butyne (186)<sup>100</sup>

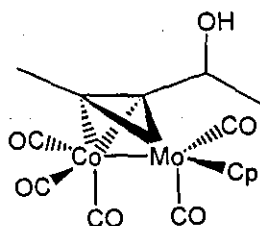


Molybdenum cyclopentadienyl tricarbonyl dimer (1.160 g, 2.40 mmol) was dissolved in dry THF (30 mL) in a flame-dried Schlenk flask under an atmosphere of nitrogen. To this was added K-Selectride (4.80 mL, 4.80 mmol, 1.0 M in THF) and the mixture was then stirred for 1.0 h. Dicobalt hexacarbonyl 2-butyne diethyl acetal (1.950 g, 4.60 mmol) in THF (2 x 5 mL) was added and the reaction mixture, then refluxed for 2.0 h.

The crude product was cooled, filtered through a plug of celite and silica, concentrated *in vacuo* and purified by flash silica chromatography eluting in petroleum ether-diethyl ether (15:1 v/v) to yield the *title complex* as a red/orange oil (1.680 g, 86%), (Found: C, 38.76; H, 2.12%;  $M^+$ , 429.8787.  $C_{14}H_9O_6CoMo$  requires C, 39.28; H, 2.12%;  $M$ , 429.8787);  $\nu_{max}$  (film)/ $cm^{-1}$  2058, 1992, 1901 ( $C\equiv O$ ), 1648 ( $C=O$ );  $\delta_H$  (250 MHz;  $CDCl_3$ ) 2.75 (3H, s,  $CH_3$ ), 5.41 (5H, s,  $CpH$ ), 10.08 (1H, s,  $CHO$ );  $\delta_c$  (100 MHz;  $CDCl_3$ ) 21.4 ( $CH_3$ ), 82.0 ( $CCH_3$ ), 90.9 ( $CpC$ ), 99.9 ( $CCHO$ ), 194.0 ( $CHO$ ), peak absent ( $Co(CO)_3$ ), 222.2, 224.2 ( $MoCp(CO)_2$ );  $m/z$  430 ( $M^+$ , 35%), 402 (73), 374 (100), 346 (31).

**Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-pent-3-yn-2-ol**

**(194)<sup>100</sup>**

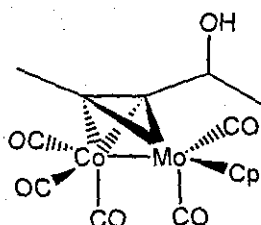


Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-butynal (0.575 g, 1.34 mmol) in THF (2 x 10 mL) was added to a flame-dried Schlenk flask under an atmosphere of nitrogen and cooled to  $-78^\circ C$ . Methylmagnesium bromide (2.24 mL, 6.71 mmol, 3.0 M in THF) was added dropwise down the inside of the flask and the reaction mixture was stirred for 1.5 h. Ethanol (3 mL) was then added and the mixture stirred for 5 min, subsequently warming to room temperature and dried over magnesium sulphate. The reaction mixture was filtered through a plug of celite and silica and reduced *in vacuo* to leave a red oil, which was purified by flash silica chromatography eluting in petroleum ether-diethyl ether (10:1 v/v) to yield the two separable *title complex* diastereoisomers as deep red oils ((i) 0.492 g, (ii) 0.082 g, 95%, 6:1 d.r.), (i) First eluting major diastereoisomer (Found:  $M^+-CO$ , 417.9140.  $C_{15}H_{13}O_6CoMo$  requires  $M-CO$ , 417.9149);  $\nu_{max}$  (film)/ $cm^{-1}$  3450 (O-H), 2044, 1973, 1929 ( $C\equiv O$ );  $\delta_H$  (250 MHz;  $CDCl_3$ ) 1.41 (3H, d,  $J$  6.4 Hz,  $CHCH_3$ ), 1.51 (1H, d,  $J$  5.5 Hz,  $CHOH$ ), 2.69 (3H, s,  $CCH_3$ ), 4.73-4.75 (1H, m,  $CHCH_3$ ), 5.43 (5H, s,  $CpH$ );  $\delta_c$  (100 MHz;  $CDCl_3$ ) 19.2 ( $CCH_3$ ), 24.5 ( $CHCH_3$ ), 70.8 ( $CH_3CH$ ), 89.1 ( $CpC$ ), 93.5

(CH<sub>3</sub>C), 96.6 (CH<sub>3</sub>CC), peak absent (Co(CO)<sub>3</sub>), 223.4, 225.3 (MoCp(CO)<sub>2</sub>); *m/z* 446 (M<sup>+</sup>, 12%), 418 (32), 390 (100), 362 (50), 334 (78). (ii) Second eluting minor diastereoisomer δ<sub>H</sub> (250 MHz; CDCl<sub>3</sub>) 1.28 (3H, d, *J* 6.3 Hz, CHCH<sub>3</sub>), 1.65 (1H, br s, CHOH), 2.69 (3H, s, CCH<sub>3</sub>), 5.00-5.02 (1H, m, CHCH<sub>3</sub>), 5.47 (5H, s, CpH); δ<sub>c</sub> (100 MHz; CDCl<sub>3</sub>) 19.1 (CCH<sub>3</sub>), 23.2 (CHCH<sub>3</sub>), 70.5 (CH<sub>3</sub>CH), 89.0 (CpC), 94.1 (CH<sub>3</sub>C), 97.4 (CH<sub>3</sub>CC), peak absent (Co(CO)<sub>3</sub>), 223.8, 224.5 (MoCp(CO)<sub>2</sub>).

**Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-pent-3-yn-2-ol**

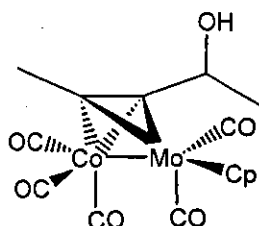
**(194)<sup>100</sup>**



Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-pent-2-yn 4-tetrafluoroborate (0.050 g, 0.10 mmol) was added to a flame-dried Schlenk flask under a nitrogen atmosphere and dissolved in dry acetonitrile (10 mL). After cooling to -40°C, water (0.10 mL) was added and the reaction mixture stirred for 0.5 h before addition of *N*-ethyl-diisopropylamine (0.02 mL, 0.17 mmol) and stirring for a further 15 min, with an immediate darkening of the orange solution to a deep red/orange colour. The reaction mixture was then filtered through a plug of celite and silica, and concentrated *in vacuo* to leave a red oil, which was purified by flash silica chromatography eluting in petroleum ether-diethyl ether (10:1 v/v) to yield the two inseparable *title complex* diastereoisomers as a red oil (0.029 g, 68%, 1:3 d.r.). Spectroscopic data were identical with those reported in the previous experiment.

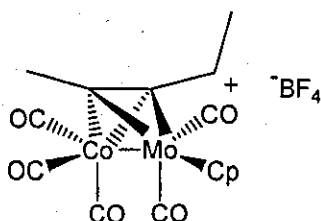
Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-pent-3-yn-2-ol

(194)<sup>100</sup>



Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-pent-1-en-3-yne (0.284 g, 0.67 mmol) in acetonitrile (15 mL) was added to a flame-dried Schlenk flask and placed under a nitrogen atmosphere. After cooling to 0°C, tetrafluoroboric acid (0.15 mL, 0.80 mmol, 0.54% diethyl ether solution) was added and the reaction mixture was stirred for 15 min, with a slight lightening in colour. Water (0.5 mL) was then added followed by *N*-ethyl-diisopropylamine (0.17 mL, 1.30 mmol) and the reaction mixture was stirred for a further 15 min, retaining its original colour. After warming to room temperature, the reaction mixture was filtered through a plug of celite and silica, then concentrated *in vacuo* to leave a red oil, which was purified by flash silica chromatography eluting in petroleum ether-diethyl ether (10:1 v/v) to yield the two inseparable *title complex* diastereoisomers as a deep red oil (0.174 g, 59%, 1:2 d.r.). Spectroscopic data were identical with those reported in the previous experiment.

Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-pent-2-yn 4-  
tetrafluoroborate (201)<sup>96</sup>

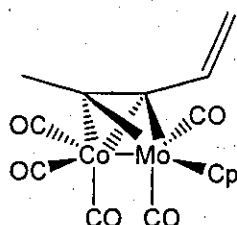


Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-pent-3-yn-2-ol (0.220 g, 0.50 mmol) was added to a flame-dried Schlenk flask and placed under a nitrogen atmosphere. After dissolving in diethyl ether (10 mL) and stirring for 2 min, tetrafluoroboric acid (0.10 mL, 0.75 mmol, 0.54% diethyl ether solution) in diethyl

ether (up to 1 mL) was then added dropwise and the reaction mixture was stirred for 0.5 h, with an immediate precipitation of an orange solid. The *title compound* was filtered and isolated as an orange solid (0.222 g, 87%), mp 108-109°C (dec); (Found:  $M^+-BF_4$ , 428.9071.  $C_{15}H_{12}O_5BCoF_4Mo$  requires  $M-BF_4$ , 428.9079);  $\nu_{max}$  (KBr)/ $cm^{-1}$  2087, 2050, 1975, 1934 ( $C\equiv O$ );  $m/z$  429 ( $M^+-BF_4$ , 56%), 401 (100), 373 (43), 345 (31), 317 (25), 289 (18).

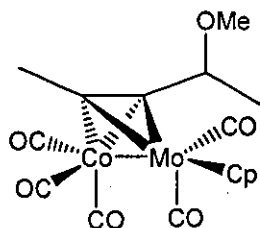
**Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-pent-1-en-3-yne**

**(211)**



Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-pent-2-yn 4-tetrafluoroborate (0.422 g, 0.80 mmol) was added to a flame-dried Schlenk flask under a nitrogen atmosphere and dissolved in dry acetonitrile (20 mL). After stirring for 2 min, *N*-ethyldiisopropylamine (0.21 mL, 1.60 mmol) was added and the reaction mixture was stirred for 0.5 h, with an immediate darkening of the orange solution to a deep red/orange colour. The reaction mixture was then filtered through a plug of celite and silica, concentrated *in vacuo* to leave a red oil, which was purified by flash silica chromatography eluting in petroleum ether-diethyl ether (15:1 v/v) to yield the *title compound* as a red oil (0.307 g, 90%) (Found:  $M^+$ , 427.8988.  $C_{15}H_{11}O_5CoMo$  requires  $M$ , 427.8996);  $\nu_{max}$  (film)/ $cm^{-1}$  2050, 1977, 1920 ( $C\equiv O$ );  $\delta_H$  (250 MHz;  $CDCl_3$ ) 2.66 (3H, s,  $CCH_3$ ), 5.16 (1H, s,  $CCHH$ ), 5.21 (1H, app t,  $J$  3.5 Hz,  $CCHH$ ), 5.34 (5H, s,  $CpH$ ), 6.75 (1H, dd,  $J$  9.7, 26.8 Hz,  $CCH$ );  $\delta_c$  (100 MHz;  $CDCl_3$ ) 21.3 ( $CCH_3$ ), 85.2 ( $CH_3CC$ ), 91.4 ( $CpC$ ), 96.7 ( $CCCH$ ), 116.7 ( $CHCH_2$ ), 138.0 ( $CCH$ ), peak absent ( $Co(CO)_3$ ), 225.2, 226.3 ( $MoCp(CO)_2$ );  $m/z$  428 ( $M^+$ , 8%), 400 (27), 372 (100), 344 (45), 316 (43).

**Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-4-methoxy-pent-2-yne (217)**

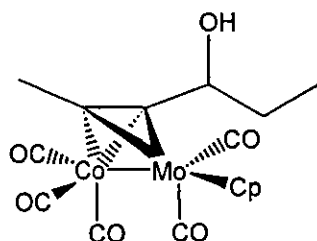


Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-pent-1-en-3-yne (0.115 g, 0.27 mmol) in acetonitrile (2 x 10 mL) was added to a flame-dried Schlenk flask and placed under a nitrogen atmosphere. After cooling to 0°C, tetrafluoroboric acid (0.45 mL, 0.33 mmol, 0.54% diethyl ether solution) was added and the reaction mixture was stirred for 15 min, with a slight lightening in colour. Methanol (1 mL) was then added followed by *N*-ethyl-diisopropylamine (0.07 mL, 0.54 mmol) and the reaction mixture was stirred for a further 15 min, retaining its original colour. After warming to room temperature, the reaction mixture was filtered through a plug of celite and silica, then concentrated *in vacuo* to leave a red oil, which was purified by flash silica chromatography eluting in petroleum ether-diethyl ether (10:1 v/v) to yield the two inseparable *title complex* diastereoisomers as a deep red oil (0.098 g, 85%, 1:2 d.r.), (Found:  $M^+$ , 459.9258.  $C_{16}H_{15}O_6CoMo$  requires  $M$ , 459.9255);  $\nu_{max}$  (film)/ $cm^{-1}$  2043, 1976, 1927 ( $C\equiv O$ ); Assigned from combined spectrum (i) Minor diastereoisomer  $\delta_H$  (250 MHz;  $CDCl_3$ ) 1.34 (3H, d,  $J$  6.3 Hz,  $CHCH_3$ ), 2.69 (3H, s,  $CCH_3$ ), 3.38 (3H, s,  $OCH_3$ ), 4.25 (1H, q,  $J$  6.2 Hz,  $CH$ ), 5.41 (5H, s,  $CpH$ );  $\delta_c$  (100 MHz;  $CDCl_3$ ) 20.8 ( $CCH_3$ ), 22.3 ( $CHCH_3$ ), 57.2 ( $OCH_3$ ), 81.0 ( $CH_3CH$ ), 90.5 ( $CpC$ ), 92.3 ( $CH_3C$ ), 98.3 ( $CH_3CC$ ), 204.5 ( $Co(CO)_3$ ), 225.4, 227.1 ( $MoCp(CO)_2$ ). (ii) Major diastereoisomer  $\delta_H$  (250 MHz;  $CDCl_3$ ) 1.23 (3H, d,  $J$  6.0 Hz,  $CHCH_3$ ), 2.69 (3H, s,  $CCH_3$ ), 3.40 (3H, s,  $OCH_3$ ), 4.46 (1H, q,  $J$  6.1 Hz,  $OCH$ ), 5.46 (5H, s,  $CpH$ );  $\delta_c$  (100 MHz;  $CDCl_3$ ) 20.6 ( $CCH_3$ ), 21.7 ( $CHCH_3$ ), 57.4 ( $OCH_3$ ), 81.7 ( $CH_3CH$ ), 90.5 ( $CpC$ ), 92.6 ( $CH_3C$ ), 98.0 ( $CH_3CC$ ), 204.5 ( $Co(CO)_3$ ), 225.8, 226.2 ( $MoCp(CO)_2$ );  $m/z$  460 ( $M^+$ , 9%), 432 (18), 404 (100), 376 (55), 348 (31).



Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-hex-4-yn-3-ol

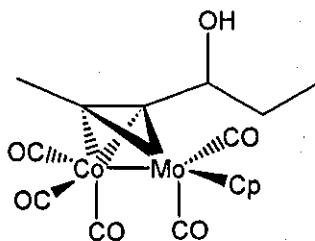
(195)<sup>100</sup>



Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-butynal (0.960 g, 2.24 mmol) in THF (2 x 15 mL) was added to a flame-dried Schlenk flask under an atmosphere of nitrogen and cooled to  $-78^{\circ}\text{C}$ . Ethylmagnesium chloride (4.50 mL, 9.00 mmol, 2.0 M in THF) was added dropwise down the inside of the flask and the reaction mixture was stirred for 1.5 h. Ethanol (3 mL) was then added and the mixture stirred for 5 min, subsequently warmed to room temperature and dried over magnesium sulphate. The reaction mixture was then filtered through a plug of celite and silica and reduced *in vacuo* to leave a red oil, which was purified by flash silica chromatography eluting in petroleum ether-diethyl ether (10:1 v/v) to yield the two separable *title complex* diastereoisomers as deep red oils (0.950 g, 0.095 g, 96%, 10:1 d.r.), (i) First eluting major diastereoisomer (Found:  $\text{M}^+-\text{CO}$ , 431.9309.  $\text{C}_{16}\text{H}_{15}\text{O}_6\text{CoMo}$  requires  $\text{M}-\text{CO}$ , 431.9309);  $\nu_{\text{max}}$  (film)/ $\text{cm}^{-1}$  3470 (O-H), 2044, 1968, 1930 ( $\text{C}\equiv\text{O}$ );  $\delta_{\text{H}}$  (250 MHz;  $\text{CDCl}_3$ ) 1.05 (3H, t,  $J$  7.4 Hz,  $\text{CH}_2\text{CH}_3$ ), 1.48-1.57 (2H, m,  $\text{CH}_2\text{CH}_3$ ), 1.65 (1H, d,  $J$  2.8 Hz,  $\text{CHOH}$ ), 2.73 (3H, s,  $\text{CCH}_3$ ), 4.65-4.73 (1H, m,  $\text{CCHCH}_2$ ), 5.48 (5H, s,  $\text{CpH}$ );  $\delta_{\text{C}}$  (100 MHz;  $\text{CDCl}_3$ ) 11.0 ( $\text{CH}_2\text{CH}_3$ ), 20.4 ( $\text{CCH}_3$ ), 31.9 ( $\text{CH}_2\text{CH}_3$ ), 76.9 ( $\text{CH}_2\text{CH}$ ), 90.1 ( $\text{CpC}$ ), 94.6 ( $\text{CH}_3\text{C}$ ), 98.6 ( $\text{CH}_3\text{CC}$ ), 203.7 ( $\text{Co}(\text{CO})_3$ ), 224.8, 225.5 ( $\text{MoCp}(\text{CO})_2$ );  $m/z$  460 ( $\text{M}^+$ , 5%), 432 (25), 404 (100), 376 (55), 348 (60). (ii) Second eluting minor diastereoisomer (Found:  $\text{M}^+-\text{CO}$ , 431.9309.  $\text{C}_{16}\text{H}_{15}\text{O}_6\text{CoMo}$  requires  $\text{M}-\text{CO}$ , 431.9309);  $\nu_{\text{max}}$  (film)/ $\text{cm}^{-1}$  3464 (O-H), 2040, 1972, 1932 ( $\text{C}\equiv\text{O}$ );  $\delta_{\text{H}}$  (250 MHz;  $\text{CDCl}_3$ ) 1.09 (3H, t,  $J$  7.4 Hz,  $\text{CH}_2\text{CH}_3$ ), 1.48-1.65 (3H, m,  $\text{CH}_2\text{CH}_3$ ,  $\text{CHOH}$ ), 2.71 (3H, s,  $\text{CCH}_3$ ), 4.38-4.46 (1H, m,  $\text{CCHCH}_2$ ), 5.43 (5H, s,  $\text{CpH}$ );  $\delta_{\text{C}}$  (100 MHz;  $\text{CDCl}_3$ ) 11.6 ( $\text{CH}_2\text{CH}_3$ ), 21.0 ( $\text{CCH}_3$ ), 33.3 ( $\text{CH}_2\text{CH}_3$ ), 77.7 ( $\text{CH}_2\text{CH}$ ), 90.5 ( $\text{CpC}$ ), 94.2 ( $\text{CH}_3\text{C}$ ), 98.1 ( $\text{CH}_3\text{CC}$ ), 204.7 ( $\text{Co}(\text{CO})_3$ ), 224.9, 226.8 ( $\text{MoCp}(\text{CO})_2$ );  $m/z$  460 ( $\text{M}^+$ , 7%), 432 (22), 404 (100), 376 (45), 348 (43).

Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-hex-4-yn-3-ol

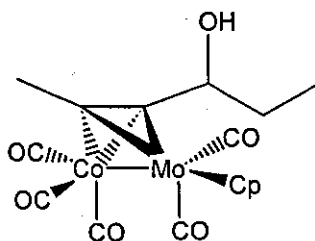
(195)<sup>100</sup>



Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-hex-2-yn 4-tetrafluoroborate (0.100 g, 0.19 mmol) was added to a flame-dried Schlenk flask under a nitrogen atmosphere and dissolved in dry acetonitrile (15 mL). After cooling to  $-40^{\circ}\text{C}$ , water (0.15 mL) was added and the reaction mixture stirred for 0.5 h before addition of *N*-ethyl-diisopropylamine (0.05 mL, 0.38 mmol) and stirring for a further 15 min, with an immediate darkening of the orange solution to a deep red/orange colour. The reaction mixture was then filtered through a plug of celite and silica, and concentrated *in vacuo* to leave a red oil, which was purified by flash silica chromatography eluting in petroleum ether-diethyl ether (10:1 v/v) to yield the two inseparable *title complex* diastereoisomers as a red oil (0.053 g, 61%, 1:5 d.r.). Spectroscopic data were identical with those reported in the previous experiment.

Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-hex-4-yn-3-ol

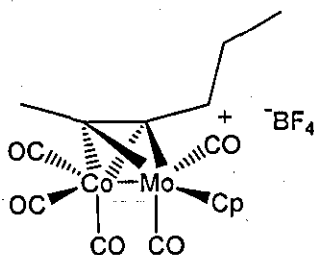
(195)<sup>100</sup>



Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-hex-2-ene (0.185 g, 0.42 mmol) in acetonitrile (15 mL) was added to a flame-dried Schlenk flask and placed under a nitrogen atmosphere. After cooling to  $0^{\circ}\text{C}$ , tetrafluoroboric acid (0.10 mL, 0.63 mmol, 0.54% diethyl ether solution) was added and the reaction mixture was

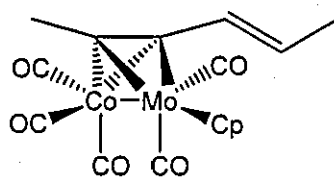
stirred for 15 min, with a slight lightening in colour. Water (0.5 mL) was then added followed by *N*-ethyldiisopropylamine (0.10 mL, 0.84 mmol) and the reaction mixture was stirred for a further 15 min, retaining its original colour. After warming to room temperature, the reaction mixture was filtered through a plug of celite and silica, then concentrated *in vacuo* to leave a red oil, which was purified by flash silica chromatography eluting in petroleum ether-diethyl ether (10:1 v/v) to yield the two inseparable *title complex* diastereoisomers as a deep red oil (0.118 g, 61%, 1:5 d.r.). Spectroscopic data were identical with those reported in the previous experiment.

**Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-hex-2-yn 4-tetrafluoroborate (202)<sup>96</sup>**



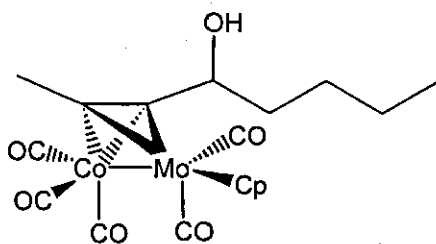
Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-hex-4-yn-3-ol (0.460 g, 1.01 mmol) was added to a flame-dried Schlenk flask under a nitrogen atmosphere and dissolved in diethyl ether (20 mL). After stirring for 2 min, tetrafluoroboric acid (0.14 mL, 2.02 mmol, 0.54% diethyl ether solution) in diethyl ether (up to 1 mL) was added dropwise and the reaction mixture was stirred for 0.5 h, with an immediate precipitation of an orange solid. The *title compound* was filtered and isolated as an orange solid (0.431 g, 81%), mp 119-120°C (dec); (Found: C, 36.3; H, 2.6%;  $M^+-BF_4$ , 442.9227.  $C_{16}H_{14}O_5BCoF_4Mo$  requires C, 36.4; H, 2.7%;  $M-BF_4$ , 442.9227);  $\nu_{max}$  (film)/cm<sup>-1</sup> 2090, 2040, 1933 (C≡O);  $m/z$  443 ( $M^+-BF_4$ , 69%), 415 (100), 387 (33), 359 (39), 331 (27), 303 (18).

**Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-hex-2-enyne (212)**



Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-hex-2-yn 4-tetrafluoroborate (0.431 g, 0.82 mmol) was added to a flame-dried Schlenk flask under a nitrogen atmosphere and dissolved in dry acetonitrile (20 mL). After stirring for 2 min, *N*-ethyldiisopropylamine (0.21 mL, 1.64 mmol) was added and the reaction mixture was stirred for 0.5 h, with an immediate darkening of the orange solution to a deep red/orange colour. The reaction mixture was then filtered through a plug of celite and silica, and concentrated *in vacuo* to leave a red oil, which was purified by flash silica chromatography eluting in petroleum ether-diethyl ether (10:1 v/v) to yield the *title complex* as a red oil (0.274 g, 76%) (Found:  $M^+$ , 441.9149.  $C_{16}H_{13}O_5CoMo$  requires  $M$ , 441.9157);  $\nu_{max}$  (film)/ $cm^{-1}$  2045, 1968, 1885 (C $\equiv$ O);  $\delta_H$  (250 MHz;  $CDCl_3$ ) 1.82 (3H, d,  $J$  6.2 Hz, CHCH $_3$ ), 2.65 (3H, s, CCH $_3$ ), 5.34 (5H, s, CpH), 5.73 (1H, app q,  $J$  6.6, 14.4 Hz, CHCHCH $_3$ ), 6.42 (1H, d,  $J$  14.8 Hz, CCHCH);  $\delta_C$  (100 MHz;  $CDCl_3$ ) 18.4 (CHCH $_3$ ), 21.2 (CCH $_3$ ), 88.9 (CH $_3$ CC), 90.9 (CpC), 95.0 (CCCH), 129.1 (CHCHCH $_3$ ), 130.7 (CCHCH), peak absent (Co(CO) $_3$ ), 225.3, 226.3 (MoCp(CO) $_2$ );  $m/z$  442 ( $M^+$ , 6%), 414 (25), 386 (100), 354 (43), 330 (32).

**Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-oct-2-yn-4-ol**  
**(196)<sup>100</sup>**

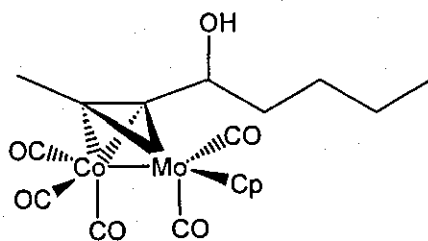


Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-butynal (0.600 g, 1.40 mmol) in THF (2 x 10 mL) was added to a flame-dried Schlenk flask under an

atmosphere of nitrogen and cooled to  $-78^{\circ}\text{C}$ . Butyl lithium (2.25 mL, 5.60 mmol, 2.5 M in hexanes) was added dropwise down the inside of the flask and the reaction mixture was stirred for 1.5 h. Ethanol (3 mL) was then added and the mixture stirred for 5 min, subsequently warming to room temperature, and dried over magnesium sulphate. The reaction mixture was then filtered through a plug of celite and silica and then concentrated *in vacuo* to leave a red oil, which was purified by flash silica chromatography eluting in petroleum ether-diethyl ether (10:1 v/v) to yield the two inseparable *title complex* diastereoisomers as a deep red oil (0.632 g, 93%, 8:1 d.r.) (Found:  $\text{M}^+-2\text{CO}$ , 431.9662.  $\text{C}_{18}\text{H}_{19}\text{O}_6\text{CoMo}$  requires  $\text{M}-2\text{CO}$ , 431.9669);  $\nu_{\text{max}}$  (film)/ $\text{cm}^{-1}$  3464 (O-H), 2045, 1976, 1931 ( $\text{C}\equiv\text{O}$ ); Assigned from combined spectrum (i) Major diastereoisomer  $\delta_{\text{H}}$  (250 MHz;  $\text{CDCl}_3$ ) 0.92 (3H, t,  $J$  6.9 Hz,  $\text{CH}_2\text{CH}_3$ ), 1.20-1.66 (7H, m,  $\text{CHOH}$ ,  $\text{CH}(\text{CH}_2)_3\text{CH}_3$ ), 2.70 (3H, s,  $\text{CCH}_3$ ), 4.46-4.53 (1H, m,  $\text{CHCH}_3$ ), 5.43 (5H, s,  $\text{CpH}$ );  $\delta_{\text{C}}$  (100 MHz;  $\text{CDCl}_3$ ) 13.0 ( $\text{CH}_2\text{CH}_3$ ), 19.6 ( $\text{CCH}_3$ ), 21.6 ( $\text{CH}_2\text{CH}_3$ ), 27.7 ( $\text{CHCH}_2\text{CH}_2$ ), 38.7 ( $\text{CHCH}_2$ ), 74.7 ( $\text{CCH}$ ), 89.2 ( $\text{CpC}$ ), 92.3 ( $\text{CH}_3\text{C}$ ), 96.6 ( $\text{CH}_3\text{CC}$ ), peak absent ( $\text{Co}(\text{CO})_3$ ), 223.5, 225.5 ( $\text{MoCp}(\text{CO})_2$ ). (ii) Minor diastereoisomer  $\delta_{\text{H}}$  (250 MHz;  $\text{CDCl}_3$ ) 0.91 (3H, t,  $J$  6.9 Hz,  $\text{CH}_2\text{CH}_3$ ), 1.20-1.66 (7H, m,  $\text{CHOH}$ ,  $\text{CH}(\text{CH}_2)_3\text{CH}_3$ ), 2.72 (3H, s,  $\text{CCH}_3$ ), 4.75-4.81 (1H, m,  $\text{CHCH}_3$ ), 5.47 (5H, s,  $\text{CpH}$ );  $\delta_{\text{C}}$  (100 MHz;  $\text{CDCl}_3$ ) 13.0 ( $\text{CH}_2\text{CH}_3$ ), 19.4 ( $\text{CCH}_3$ ), 21.6 ( $\text{CH}_2\text{CH}_3$ ), 27.5 ( $\text{CHCH}_2\text{CH}_2$ ), 37.6 ( $\text{CHCH}_2$ ), 74.3 ( $\text{CCH}$ ), 89.1 ( $\text{CpC}$ ), 93.2 ( $\text{CH}_3\text{C}$ ), 97.5 ( $\text{CH}_3\text{CC}$ ), peak absent ( $\text{Co}(\text{CO})_3$ ), 223.9, 224.5 ( $\text{MoCp}(\text{CO})_2$ );  $m/z$  460 ( $\text{M}^+$ , 4%), 432 (17), 404 (22), 376 (22).

**Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-oct-2-yn-4-ol**

**(196)<sup>100</sup>**

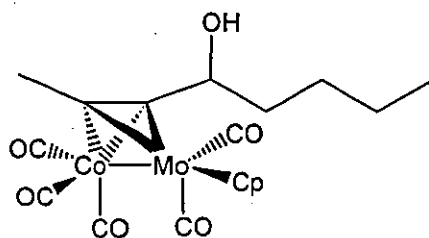


Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-oct-2-yn 4-tetrafluoroborate (0.050 g, 0.10 mmol) was added to a flame-dried Schlenk flask under a nitrogen atmosphere and dissolved in dry acetonitrile (10 mL). After cooling to –

40°C, water (0.10 mL) was added and the reaction mixture stirred for 0.5 h before addition of *N*-ethyldiisopropylamine (0.02 mL, 0.17 mmol) and stirring for a further 15 min, with an immediate darkening of the orange solution to a deep red/orange colour. The reaction mixture was then filtered through a plug of celite and silica, and concentrated *in vacuo* to leave a red oil, which was purified by flash silica chromatography eluting in petroleum ether-diethyl ether (10:1 v/v) to yield the two inseparable *title complex* diastereoisomers as a red oil (0.029 g, 66%, 1:4.5 d.r.). Spectroscopic data were identical with those reported in the previous experiment.

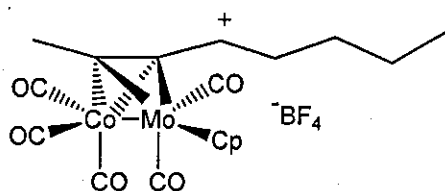
**Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-oct-2-yn-4-ol**

**(196)<sup>100</sup>**



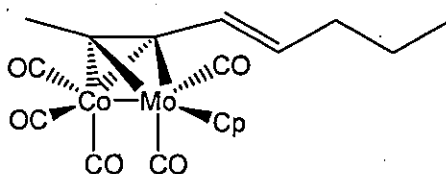
Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-oct-2-ene (0.170 g, 0.36 mmol) in acetonitrile (15 mL) was added to a flame-dried Schlenk flask and placed under a nitrogen atmosphere. After cooling to 0°C, tetrafluoroboric acid (0.10 mL, 0.63 mmol, 0.54% diethyl ether solution) was added and the reaction mixture was stirred for 15 min, with a slight lightening in colour. Water (0.5 mL) was then added followed by *N*-ethyldiisopropylamine (0.09 mL, 0.72 mmol) and the reaction mixture was stirred for a further 15 min, retaining its original colour. After warming to room temperature, the reaction mixture was filtered through a plug of celite and silica, then concentrated *in vacuo* to leave a red oil, which was purified by flash silica chromatography eluting in petroleum ether-diethyl ether (10:1 v/v) to yield the two inseparable *title complex* diastereoisomers as a deep red oil (0.116 g, 60%, 1:5 d.r.). Spectroscopic data were identical with those reported in the previous experiment.

**Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-oct-2-yn 4-tetrafluoroborate (203)<sup>96</sup>**



Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-oct-2-yn-4-ol (0.455 g, 0.94 mmol) was added to a flame-dried Schlenk flask under a nitrogen atmosphere and dissolved in diethyl ether (15 mL). After stirring for 2 min, tetrafluoroboric acid (0.16 mL, 1.13 mmol, 0.54% diethyl ether solution) in diethyl ether (up to 1 mL) was then added dropwise and the reaction mixture was stirred for 0.5 h, with an immediate precipitation of the orange solid. The *title compound* was filtered and isolated as an orange solid (0.438 g, 84%), mp 94-95°C (dec); (Found: C, 38.5; H, 3.2%;  $M^+-BF_4$ , 470.9532.  $C_{18}H_{18}O_5BCoF_4Mo$  requires C, 38.9; H, 3.3%;  $M-BF_4$ , 470.9540);  $\nu_{max}$  (KBr)/ $cm^{-1}$  2045, 1975, 1932 ( $C\equiv O$ );  $m/z$  471 ( $M^+-BF_4$ , 53%), 443 (100), 415 (49), 387 (37), 359 (45), 331 (29).

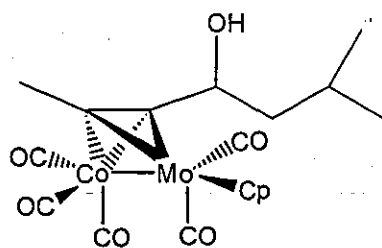
**Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-oct-4-enyne (213)**



Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-oct-2-yn 4-tetrafluoroborate (0.315 g, 0.57 mmol) was added to a flame-dried Schlenk flask under a nitrogen atmosphere and dissolved in dry acetonitrile (20 mL). After stirring for 2 min, *N*-ethyldiisopropylamine (0.15 mL, 1.11 mmol) was added and the reaction mixture was stirred for 0.5 h, with an immediate darkening of the orange solution to a deep red/orange colour. The reaction mixture was then filtered through a plug of celite and silica, concentrated *in vacuo* to leave a red oil, which was purified by flash silica chromatography eluting in petroleum ether-diethyl ether (10:1 v/v) to yield the *title*

*complex* as a red oil (0.221 g, 83%) (Found:  $M^+$ , 441.9510.  $C_{18}H_{17}O_5CoMo$  requires  $M$ , 441.9513);  $\nu_{max}$  (film)/ $cm^{-1}$  2045, 1973, 1931 ( $C\equiv O$ );  $\delta_H$  (250 MHz;  $CDCl_3$ ) 0.90 (3H, t,  $J$  2.0 Hz,  $CH_2CH_3$ ), 1.44 (2H, q,  $J$  7.1 Hz,  $CH_2CH_3$ ), 2.13 (2H, q,  $J$  6.8 Hz,  $CHCH_2$ ), 2.65 (3H, s,  $CCH_3$ ), 5.33 (5H, s,  $CpH$ ), 5.64-5.76 (1H, m,  $CH_2CH$ ), 6.40 (1H, d,  $J$  14.8 Hz,  $CCH$ );  $\delta_c$  (100 MHz;  $CDCl_3$ ) 13.5 ( $CH_2CH_3$ ), 21.3 ( $CCH_3$ ), 22.7 ( $CH_2CH_3$ ), 34.9 ( $CHCH_2$ ), 89.5 ( $CH_3CC$ ), 91.0 ( $CpC$ ), 94.4 ( $CCCH$ ), 129.5 ( $CHCH_2$ ), 134.6 ( $CCHCH$ ), peak absent ( $Co(CO)_3$ ), 225.4, 226.3 ( $MoCp(CO)_2$ );  $m/z$  442 ( $M^+$ , 27%), 414 (100), 386 (30), 358 (24).

**Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-6-methylhept-2-yn-4-ol (197)<sup>100</sup>**

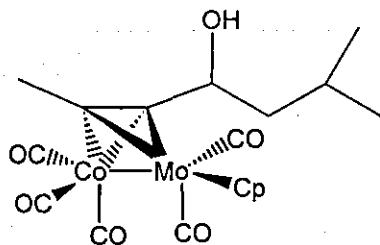


Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-butynal (0.960 g, 2.24 mmol) in THF (2 x 15 mL) was added to a flame-dried Schlenk flask under an atmosphere of nitrogen and cooled to  $-78^\circ C$ . Isobutylmagnesium chloride (4.50 mL, 9.00 mmol, 2.0 M in THF) was added dropwise down the inside of the flask and the reaction mixture was stirred for 1.5 h. Ethanol (3 mL) was then added and the mixture stirred for 5 min, subsequently warmed to room temperature and dried over magnesium sulphate. The reaction mixture was then filtered through a plug of celite and silica and reduced *in vacuo* to leave a red oil, which was purified by flash silica chromatography eluting in petroleum ether-diethyl ether (10:1 v/v) to yield the two separable *title complex* diastereoisomers as deep red oils (1.010 g, 0.101 g, 96%, 10:1 d.r.) (i) First eluting major diastereoisomer (Found:  $M^+-CO$ , 459.9628.  $C_{18}H_{19}O_6CoMo$  requires  $M-CO$ , 459.9619);  $\nu_{max}$  (film)/ $cm^{-1}$  3464 (O-H), 2057, 2045, 1968 ( $C\equiv O$ );  $\delta_H$  (250 MHz;  $CDCl_3$ ) 0.96 (6H, d,  $J$  6.5 Hz,  $CH(CH_3)_2$ ), 1.15-1.26 (2H, m,  $CHCH_2$ ), 1.60 (1H, d,  $J$  2.8 Hz,  $CHOH$ ), 1.77-1.89 (1H, m,  $CH(CH_3)_2$ ), 2.72 (3H, s,  $CCH_3$ ), 4.86-4.90 (1H, m,  $CCHCH_2$ ), 5.48 (5H, s,  $CpH$ );  $\delta_c$  (100 MHz;  $CDCl_3$ ) 20.7, 20.9 ( $CH(CH_3)_2$ ), 22.7



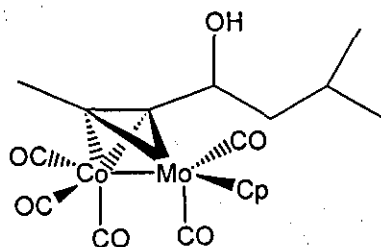
(CCH<sub>3</sub>), 24.2 (CH(CH<sub>3</sub>)<sub>2</sub>), 48.2 (CHCH<sub>2</sub>), 72.8 (CH<sub>3</sub>CH), 89.3 (CpC), 93.5 (CH<sub>3</sub>C), 96.6 (CH<sub>3</sub>CC), peak absent (Co(CO)<sub>3</sub>), 223.5, 225.4 (MoCp(CO)<sub>2</sub>); *m/z* 488 (M<sup>+</sup>, 8%), 460 (19), 432 (100), 404 (48), 376 (50). (ii) Second eluting minor diastereoisomer (Found: M<sup>+</sup>, 487.9580. C<sub>18</sub>H<sub>19</sub>O<sub>6</sub>CoMo requires M, 487.9573);  $\nu_{\max}$  (film)/cm<sup>-1</sup> 3461 (O-H), 2059, 2042, 1967 (C≡O);  $\delta_{\text{H}}$  (250 MHz; CDCl<sub>3</sub>) 0.96 (3H, d, *J* 2.7 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 0.99 (3H, d, *J* 2.7 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.21 (2H, t, *J* 7.1 Hz, CHCH<sub>2</sub>), 1.60 (1H, d, *J* 2.7 Hz, CHOH), 1.86-1.96 (1H, m, CH(CH<sub>3</sub>)<sub>2</sub>), 2.70 (3H, s, CCH<sub>3</sub>), 4.55-4.63 (1H, m, CCHCH<sub>2</sub>), 5.43 (5H, s, CpH);  $\delta_{\text{C}}$  (100 MHz; CDCl<sub>3</sub>) 19.4, 20.9 (CH(CH<sub>3</sub>)<sub>2</sub>), 22.5 (CCH<sub>3</sub>), 23.9 (CH(CH<sub>3</sub>)<sub>2</sub>), 47.1 (CCH<sub>2</sub>), 72.4 (CH<sub>3</sub>CH), 89.2 (CpC), 93.5 (CH<sub>3</sub>C), 96.6 (CH<sub>3</sub>CC), peak absent (Co(CO)<sub>3</sub>), 223.8, 224.5 (MoCp(CO)<sub>2</sub>); *m/z* 488 (M<sup>+</sup>, 9%), 460 (20), 432 (100), 404 (45), 376 (50).

**Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-6-methylhept-2-yn-4-ol (197)**<sup>100</sup>



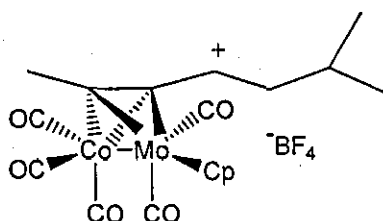
Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-6-methylhept-2-yn 4-tetrafluoroborate (0.099 g, 0.18 mmol) was added to a flame-dried Schlenk flask under a nitrogen atmosphere and dissolved in dry acetonitrile (15 mL). After cooling to -40°C, water (0.20 mL) was added and the reaction mixture stirred for 0.5 h before addition of *N*-ethyldiisopropylamine (0.05 mL, 0.36 mmol) and stirring for a further 15 min, with an immediate darkening of the orange solution to a deep red/orange colour. The reaction mixture was then filtered through a plug of celite and silica, and concentrated *in vacuo* to leave a red oil, which was purified by flash silica chromatography eluting in petroleum ether-diethyl ether (10:1 v/v) to yield the two inseparable *title complex* diastereoisomers as a red oil (0.062 g, 70%, 1:6 d.r.). Spectroscopic data were identical with those reported in the previous experiment.

**Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-6-methylhept-2-yn-4-ol (197)<sup>100</sup>**



Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-6-methylhept-2-yn-4-ol (0.040 g, 0.09 mmol) in acetonitrile (10 mL) was added to a flame-dried Schlenk flask and placed under a nitrogen atmosphere. After cooling to 0°C, tetrafluoroboric acid (0.02 mL, 0.13 mmol, 0.54% diethyl ether solution) was added and the reaction mixture was stirred for 15 min, with a slight lightening in colour. Water (0.3 mL) was then added followed by *N*-ethyl-diisopropylamine (0.02 mL, 0.18 mmol) and the reaction mixture was stirred for a further 15 min, retaining its original colour. After warming to room temperature, the reaction mixture was filtered through a plug of celite and silica, then concentrated *in vacuo* to leave a red oil, which was purified by flash silica chromatography eluting in petroleum ether-diethyl ether (10:1 v/v) to yield the two inseparable *title complex* diastereoisomers as a deep red oil (0.027 g, 65%, 1:5 d.r.). Spectroscopic data were identical with those reported in the previous experiment.

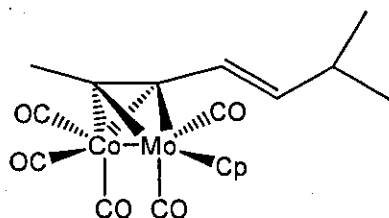
**Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-6-methylhept-2-yn-4-ol-tetrafluoroborate (205)<sup>96</sup>**



Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-6-methylhept-2-yn-4-ol (1.050 g, 2.16 mmol) was added to a flame-dried Schlenk flask under a nitrogen atmosphere and dissolved in diethyl ether (25 mL). After stirring for 2 min, tetrafluoroboric acid (0.53 mL, 3.24 mmol, 0.54% diethyl ether solution) in diethyl

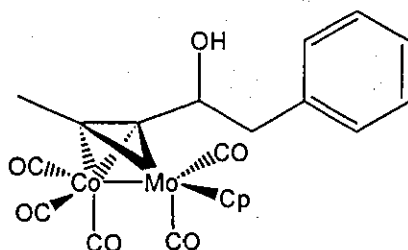
ether (up to 2 mL) was added dropwise and the reaction mixture was stirred for 0.5 h, with an immediate precipitation of the orange solid. The *title compound* was filtered and isolated as an orange solid (0.859 g, 85%), mp 107.5-108.6°C (dec); (Found: C, 37.7; H, 3.2%;  $M^+-BF_4$ , 470.9540.  $C_{18}H_{18}O_5BCoF_4Mo$  requires C, 38.9; H, 3.3%;  $M-BF_4$ , 470.9543);  $\nu_{max}$  (film)/ $cm^{-1}$  2090, 2055, 2041 ( $C\equiv O$ );  $m/z$  471 ( $M^+-BF_4$ , 63%), 443 (100), 415 (37), 387 (30), 359 (29), 331 (13).

**Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-6-methylhept-4-  
enyne (214)**



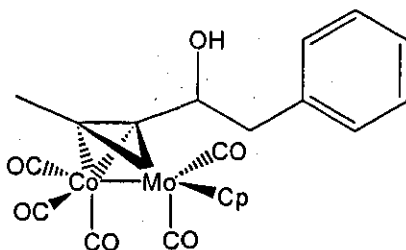
Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-6-methyl-hept-2-yn 4-tetrafluoroborate (0.585 g, 1.05 mmol) was added to a flame-dried Schlenk flask under a nitrogen atmosphere and dissolved in dry acetonitrile (20 mL). After stirring for 2 min, *N*-ethyldiisopropylamine (0.20 mL, 1.58 mmol) was added and the reaction mixture was stirred for 0.5 h, with an immediate darkening of the orange solution to a deep red/orange colour. The mixture was then filtered through a plug of celite and silica, concentrated *in vacuo* to leave a red oil, which was purified by flash silica chromatography eluting in petroleum ether-diethyl ether (10:1 v/v) to yield the *title complex* as a red oil (0.424 g, 86%) (Found:  $M^+$ , 469.9462.  $C_{18}H_{17}O_5CoMo$  requires  $M$ , 469.9462);  $\nu_{max}$  (film)/ $cm^{-1}$  2045, 1968, 1885 ( $C\equiv O$ );  $\delta_H$  (250 MHz;  $CDCl_3$ ) 1.03 (6H, d,  $J$  6.2 Hz,  $CH(CH_3)_2$ ), 2.38-2.44 (1H, m,  $CH(CH_3)_2$ ), 2.65 (3H, s,  $CCH_3$ ), 5.32 (5H, s,  $CpH$ ), 5.68 (1H, dd,  $J$  6.9, 21.7 Hz,  $CHCHCH$ ), 6.34 (1H, d,  $J$  15.0 Hz,  $CCHCH$ );  $\delta_C$  (100 MHz;  $CDCl_3$ ) 21.4 ( $CCH_3$ ), 22.6, 22.7 ( $CH(CH_3)_2$ ), 31.5 ( $CH(CH_3)_2$ ), 90.0 ( $CH_3CC$ ), 91.1 ( $CpC$ ), 93.9 ( $CCCH$ ), 126.2 ( $CHCHCH$ ), 141.8 ( $CCHCH$ ), peak absent ( $Co(CO)_3$ ), 225.5, 226.3 ( $MoCp(CO)_2$ );  $m/z$  470 ( $M^+$ , 10%), 442 (20), 414 (100), 386 (28), 358 (17).

**Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-1-phenylpent-3-yn-2-ol (198)**



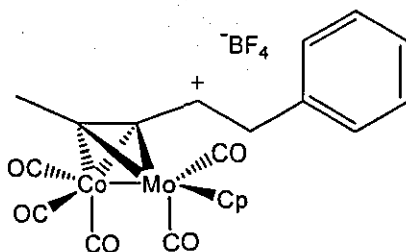
Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-butynal (0.955 g, 2.23 mmol) in THF (2 x 15 mL) was added to a flame-dried Schlenk flask under an atmosphere of nitrogen and cooled to  $-78^{\circ}\text{C}$ . Benzylmagnesium chloride (4.5 mL, 8.92 mmol, 2.0 M in THF) was added dropwise down the inside of the flask and the reaction mixture was stirred for 1.5 h. Ethanol (3 mL) was then added and the mixture stirred for 5 min, subsequently warmed to room temperature and dried over solid magnesium sulphate. The reaction mixture was then filtered through a plug of celite and silica and concentrated *in vacuo* to leave a red oil, which was purified by flash silica chromatography eluting in petroleum ether-diethyl ether (10:1 v/v) to yield the two inseparable *title complex* diastereoisomers as a deep red oil (1.140 g, 96%, 10:1 d.r.) (Found:  $\text{M}^+-3\text{CO}$ , 437.9563.  $\text{C}_{21}\text{H}_{17}\text{O}_6\text{CoMo}$  requires  $\text{M}-3\text{CO}$ , 437.9568);  $\nu_{\text{max}}$  (film)/ $\text{cm}^{-1}$  3433 (O-H), 2044, 1973, 1928 ( $\text{C}\equiv\text{O}$ ); Assigned from combined spectrum (i) First eluting major diastereoisomer  $\delta_{\text{H}}$  (250 MHz;  $\text{CDCl}_3$ ) 1.71 (1H, d,  $J$  4.4 Hz,  $\text{CHOH}$ ), 2.71 (3H, s,  $\text{CCH}_3$ ), 3.01 (2H, dd,  $J$  2.6, 13.9 Hz,  $\text{CHCH}_2$ ), 4.74-4.78 (1H, m,  $\text{CCHCH}_2$ ), 5.44 (5H, s,  $\text{CpH}$ ), 7.28-7.36 (5H, m,  $\text{ArCH}$ );  $\delta_{\text{C}}$  (100 MHz;  $\text{CDCl}_3$ ) 20.8 ( $\text{CCH}_3$ ), 46.9 ( $\text{ArCH}_2$ ), 77.0 ( $\text{CH}_2\text{CH}$ ), 90.7 ( $\text{CpC}$ ), 92.9 ( $\text{CH}_3\text{C}$ ), 98.2 ( $\text{CH}_3\text{CC}$ ), 127.1 (2C, s,  $\text{ArCH}$ ), 129.1 ( $\text{ArCH}$ ), 129.8 (2C, s,  $\text{ArCH}$ ), 139.0 ( $\text{ArC}$ ), 204.8 ( $\text{Co}(\text{CO})_3$ ), 225.1, 226.9 ( $\text{MoCp}(\text{CO})_2$ );  $m/z$  438 ( $\text{M}^+-3\text{CO}$ , 100%), 410 (28), 382 (22). (ii) Second eluting minor diastereoisomer  $\delta_{\text{H}}$  (250 MHz;  $\text{CDCl}_3$ ) 1.79 (1H, d,  $J$  2.8 Hz,  $\text{CHOH}$ ), 2.71 (3H, s,  $\text{CCH}_3$ ), 2.85 (2H, dd,  $J$  2.8, 13.6 Hz,  $\text{CHCH}_2$ ), 5.01-5.05 (1H, m,  $\text{CCHCH}_2$ ), 5.52 (5H, s,  $\text{CpH}$ ), 7.28-7.36 (5H, m,  $\text{ArCH}$ );  $\delta_{\text{C}}$  (100 MHz;  $\text{CDCl}_3$ ) 20.7 ( $\text{CCH}_3$ ), 45.8 ( $\text{ArCH}_2$ ), 76.9 ( $\text{CH}_2\text{CH}$ ), 90.6 ( $\text{CpC}$ ), 93.5 ( $\text{CH}_3\text{C}$ ), 98.6 ( $\text{CH}_3\text{CC}$ ), 127.5 (2C, s,  $\text{ArCH}$ ), 129.0 ( $\text{ArCH}$ ), 129.8 (2C, s,  $\text{ArCH}$ ), 138.8 ( $\text{ArC}$ ), 204.8 ( $\text{Co}(\text{CO})_3$ ), 225.5, 226.0 ( $\text{MoCp}(\text{CO})_2$ ).

**Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-1-phenylpent-3-yn-2-ol (198)<sup>100</sup>**



Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-5-phenylpent-4-yn-2-ol (0.089 g, 0.18 mmol) in acetonitrile (10 mL) was added to a flame-dried Schlenk flask and placed under a nitrogen atmosphere. After cooling to 0°C, tetrafluoroboric acid (0.04 mL, 0.27 mmol, 0.54% diethyl ether solution) was added and the reaction mixture was stirred for 15 min, with a slight lightening in colour. Water (0.5 mL) was then added followed by *N*-ethyldiisopropylamine (0.05 mL, 0.36 mmol) and the reaction mixture was stirred for a further 15 min, retaining its original colour. After warming to room temperature, the reaction mixture was filtered through a plug of celite and silica, then concentrated *in vacuo* to leave a red oil, which was purified by flash silica chromatography eluting in petroleum ether-diethyl ether (10:1 v/v) to yield the two inseparable *title complex* diastereoisomers as a deep red oil (0.029 g, 30%, 1:1 d.r.). Spectroscopic data were identical with those reported in the previous experiment.

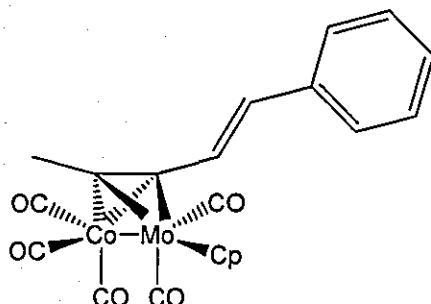
**Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-5-phenylpent-2-yn-4-tetrafluoroborate (204)<sup>96</sup>**



Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-1-phenylpent-3-yn-2-ol (0.238 g, 0.46 mmol) was added to a flame-dried Schlenk flask under a nitrogen atmosphere and dissolved in diethyl ether (15 mL). After stirring for 2 min,

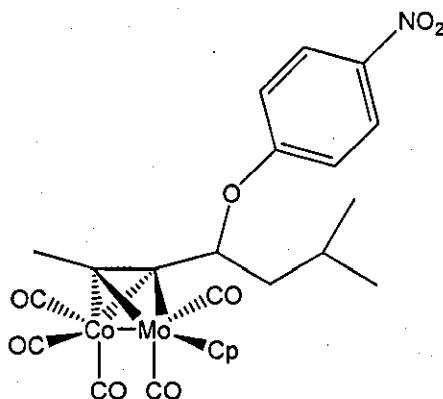
tetrafluoroboric acid (0.13 mL, 0.92 mmol, 0.54% diethyl ether solution) in diethyl ether (up to 1 mL) was added dropwise and the reaction mixture was stirred for 30 min, with an immediate precipitation of the orange solid. The *title compound* was filtered and isolated as an orange solid (0.252 g, 93%), mp 97-98°C (dec);  $\nu_{\max}$  (film)/cm<sup>-1</sup> 2057, 1992, 1946 (C≡O).

**Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-5-phenylpent-4-  
enyne (207)**



Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-5-phenyl-pent-2-yn-4-tetrafluoroborate (0.252 g, 0.43 mmol) was added to a flame-dried Schlenk flask under a nitrogen atmosphere and dissolved in dry acetonitrile (20 mL). After stirring for 2 min, *N*-ethyldiisopropylamine (0.11 mL, 0.86 mmol) was added and the reaction mixture was stirred for 0.5 h, with an immediate darkening of the orange solution to a deep red/orange colour. The reaction mixture was then filtered through a plug of celite and silica and concentrated *in vacuo* to leave a red oil, which was purified by flash silica chromatography eluting in petroleum ether-diethyl ether (10:1 v/v) to yield the *title complex* as a red oil (0.232 g, 94%) (Found:  $M^+ - CO$ , 475.9352.  $C_{21}H_{15}O_5CoMo$  requires 475.9361);  $\nu_{\max}$  (film)/cm<sup>-1</sup> 2045, 1974, 1932 (C≡O);  $\delta_H$  (250 MHz;  $CDCl_3$ ) 2.74 (3H, s,  $CCH_3$ ), 5.37 (5H, s,  $CpH$ ), 6.55 (1H, d,  $J$  15.3 Hz,  $CCHCH$ ), 7.16-7.43 (6H, m,  $CHCHAr$ ,  $ArCH$ );  $\delta_c$  (100 MHz;  $CDCl_3$ ) 21.2 ( $CCH_3$ ), 87.3 ( $CH_3CC$ ), 91.0 ( $CpC$ ), 96.8 ( $CCCH$ ), 126.2 (2C, s,  $ArCH$ ), 128.7 (2C, s,  $ArCH$ ), 127.4, 130.1, 131.7 ( $CHCHCH$ ,  $CCHCH$ ,  $ArCH$ ), peak absent ( $Co(CO)_3$ ), 224.8, 226.0 ( $MoCp(CO)_2$ );  $m/z$  476 ( $M^+ - CO$ , 9%), 448 (52), 420 (28), 392 (23), 364 (53).

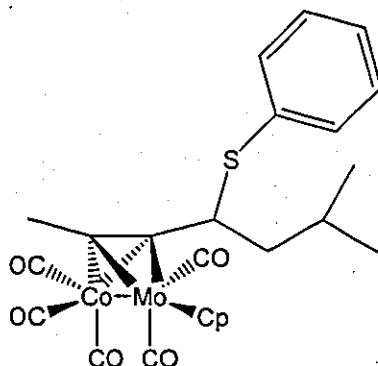
**Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-6-methyl-4-(4-nitrophenoxy)-hept-2-yne (208)**



Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-6-methylhept-2-yn 4-tetrafluoroborate (0.265 g, 0.48 mmol) was added to a flame-dried Schlenk flask under a nitrogen atmosphere and dissolved in dry acetonitrile (20 mL). After cooling to  $-40^{\circ}\text{C}$ , 4-nitrobenzyl alcohol (0.100 g, 0.71 mmol) was added and the reaction mixture stirred for 0.5 h before addition of *N*-ethyldiisopropylamine (0.12 mL, 0.96 mmol) and stirring for a further 15 min, with an immediate darkening of the orange solution to a deep red/orange colour. The reaction mixture was then filtered through a plug of celite and silica, and concentrated *in vacuo* to leave a red oil, which was purified by flash silica chromatography eluting in petroleum ether-diethyl ether (10:1 v/v) to yield the two inseparable *title complex* diastereoisomers as a red oil (0.256 g, 89%, 1:2 d.r.) (Found:  $\text{M}^+-3\text{CO}$ , 524.9892.  $\text{C}_{24}\text{H}_{22}\text{O}_8\text{CoMoN}$  requires  $\text{M}-3\text{CO}$ , 524.9884);  $\nu_{\text{max}}$  (neat film)/ $\text{cm}^{-1}$  2047, 1979, 1934 ( $\text{C}\equiv\text{O}$ ), 1591, 1340 ( $\text{NO}_2$ ), 1256 ( $\text{C}-\text{O}$ ); Assigned from combined spectrum (i) Minor diastereoisomer  $\delta_{\text{H}}$  (250 MHz;  $\text{CDCl}_3$ ) 0.93 (3H, d,  $J$  6.5 Hz,  $\text{CH}(\text{CH}_3)_2$ ), 0.99 (3H, d,  $J$  6.5 Hz,  $\text{CH}(\text{CH}_3)_2$ ), 1.43-1.53 (1H, m,  $\text{CH}(\text{CH}_3)_2$ ), 1.69-1.84 (2H, m,  $\text{CHCH}_2$ ), 2.64 (3H, s,  $\text{CCH}_3$ ), 5.44 (5H, s,  $\text{CpH}$ ), 5.65-4.69 (1H, m,  $\text{CCHCH}_2$ ), 6.94-6.99 (2H, m,  $\text{ArCH}$ ), 8.18-8.24 (2H, m,  $\text{ArCH}$ );  $\delta_{\text{C}}$  (100 MHz;  $\text{CDCl}_3$ ) 21.0 ( $\text{CCH}_3$ ), 22.2, 23.1 ( $\text{CH}(\text{CH}_3)_2$ ), 24.8 ( $\text{CH}(\text{CH}_3)_2$ ), 46.9 ( $\text{CHCH}_2$ ), 81.0 ( $\text{CCHCH}_2$ ), 88.1 ( $\text{CH}_3\text{C}$ ), 90.4 ( $\text{CpC}$ ), 98.5 ( $\text{CH}_3\text{CC}$ ), 114.8, 126.2 ( $\text{ArCH}$ ), 141.2, 163.8 ( $\text{ArC}$ ), 203.4 ( $\text{Co}(\text{CO})_3$ ), 224.8, 225.4 ( $\text{MoCp}(\text{CO})_2$ );  $m/z$  525 ( $\text{M}^+-3\text{CO}$ , 100%), 469 (20). (ii) Major diastereoisomer  $\delta_{\text{H}}$  (250 MHz;  $\text{CDCl}_3$ ) 0.91-1.00 (6H, m,  $\text{CH}(\text{CH}_3)_2$ ), 1.43-1.53 (1H, m,  $\text{CH}(\text{CH}_3)_2$ ), 1.69-1.84 (2H, m,  $\text{CHCH}_2$ ), 2.71 (3H, s,  $\text{CCH}_3$ ), 5.21 (5H, s,  $\text{CpH}$ ), 5.44-5.53 (1H, m,  $\text{CCHCH}_2$ ), 6.94-6.99 (2H, m,  $\text{ArCH}$ ),

8.18-8.24 (2H, m, ArCH);  $\delta_c$  (100 MHz;  $CDCl_3$ ) 20.7 ( $CCH_3$ ), 22.1, 23.2 ( $CH(CH_3)_2$ ), 25.0 ( $CH(CH_3)_2$ ), 47.9 ( $CHCH_2$ ), 80.2 ( $CCHCH_2$ ), 87.2 ( $CH_3C$ ), 90.1 ( $CpC$ ), 99.4 ( $CH_3CC$ ), 114.6, 126.2 (ArCH), 141.1, 163.8 (ArC), 203.4 ( $Co(CO)_3$ ), 224.4, 226.1 ( $MoCp(CO)_2$ ).

**Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-6-methyl-4-phenylthiohept-2-yne (209)**

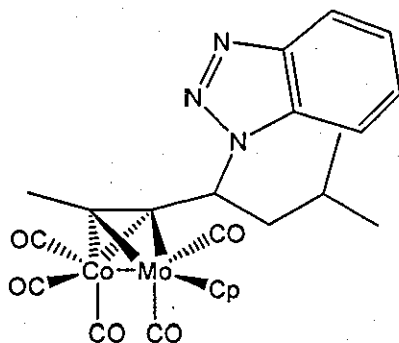


Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-6-methylhept-2-yn 4-tetrafluoroborate (0.435 g, 0.78 mmol) was added to a flame-dried Schlenk flask under a nitrogen atmosphere and dissolved in dry acetonitrile (20 mL). After cooling to  $-40^\circ C$ , thiophenol (0.12 mL, 1.17 mmol) was added and the reaction mixture stirred for 0.5 h before addition of *N*-ethyl-diisopropylamine (0.20 mL, 1.56 mmol) and stirring for a further 15 min, with an immediate darkening of the orange solution to a deep red/orange colour. The reaction mixture was then filtered through a plug of celite and silica, and concentrated *in vacuo* to leave a red oil, which was purified by flash silica chromatography eluting in petroleum ether-diethyl ether (10:1 v/v) to yield the two inseparable *title complex* diastereoisomers as a red oil (0.420 g, 93%, 1:4 d.r.) (Found:  $M^+-3CO$ , 495.9817.  $C_{24}H_{23}O_5CoMoS$  requires  $M-3CO$ , 495.9807);  $\nu_{max}$  (film)/ $cm^{-1}$  2044, 1970, 1933 ( $C\equiv O$ ); Assigned from combined spectrum (i) Minor diastereoisomer  $\delta_H$  (250 MHz;  $CDCl_3$ ) 0.91 (3H, d,  $J$  2.0 Hz,  $CH(CH_3)_2$ ), 0.93 (3H, d,  $J$  2.0 Hz,  $CH(CH_3)_2$ ), 1.56-1.72 (2H, m,  $CHCH_2$ ), 1.93-2.07 (1H, m,  $CH(CH_3)_2$ ), 2.69 (3H, s,  $CCH_3$ ), 4.46-4.50 (1H, m,  $CCHCH_2$ ), 5.20 (5H, s,  $CpH$ ), 7.20-7.41 (5H, m, ArCH);  $\delta_c$  (100 MHz;  $CDCl_3$ ) 21.5, 22.1 ( $CH(CH_3)_2$ ), 23.6 ( $CCH_3$ ), 26.5 ( $CH(CH_3)_2$ ), 48.5 ( $CHCH_2$ ), 55.2 ( $CCHCH_2$ ), 90.9 ( $CpC$ ), 92.6 ( $CH_3C$ ), 100.8 ( $CH_3CC$ ), 126.7, 129.4,



130.4 (ArCH), 138.1 (ArC), 204.8 (Co(CO)<sub>3</sub>), 225.1, 226.9 (MoCp(CO)<sub>2</sub>); *m/z* 496 (M<sup>+</sup>-3CO, 100%), 440 (65). (ii) Major diastereoisomer  $\delta_H$  (250 MHz; CDCl<sub>3</sub>) 0.84-0.94 (6H, m, CH(CH<sub>3</sub>)<sub>2</sub>), 1.56-1.72 (2H, m, CHCH<sub>2</sub>), 1.93-2.07 (1H, m, CH(CH<sub>3</sub>)<sub>2</sub>), 2.56 (3H, s, CCH<sub>3</sub>), 4.40-4.50 (1H, m, CCHCH<sub>2</sub>), 5.40 (5H, s, CpH), 7.20-7.41 (5H, m, ArCH);  $\delta_c$  (100 MHz; CDCl<sub>3</sub>) 21.4, 21.9 (CH(CH<sub>3</sub>)<sub>2</sub>), 23.8 (CCH<sub>3</sub>), 26.2 (CH(CH<sub>3</sub>)<sub>2</sub>), 48.9 (CHCH<sub>2</sub>), 54.6 (CCHCH<sub>2</sub>), 90.9 (CpC), 93.7 (CH<sub>3</sub>C), 101.7 (CH<sub>3</sub>CC), 126.8, 129.5, 130.8 (ArCH), 137.8 (ArC), 204.8 (Co(CO)<sub>3</sub>), 225.0, 227.1 (MoCp(CO)<sub>2</sub>).

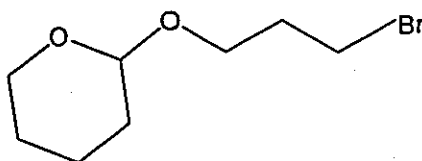
**Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-6-methyl-4-(benzotriazol-1-yl)-hept-2-yne (210)**



Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-6-methylhept-2-yn 4-tetrafluoroborate (0.250 g, 0.45 mmol) was added to a flame-dried Schlenk flask under a nitrogen atmosphere and dissolved in dry acetonitrile (20 mL). After cooling to -40°C, benzotriazole (0.080 g, 0.70 mmol) was added and the reaction mixture stirred for 0.5 h before addition of *N*-ethyldiisopropylamine (0.12 mL, 0.90 mmol) and stirring for a further 15 min, with an immediate darkening of the orange solution to a deep red/orange colour. The reaction mixture was then filtered through a plug of celite and silica, and concentrated *in vacuo* to leave a red oil, which was purified by flash silica chromatography eluting in petroleum ether-diethyl ether (10:1 v/v) to yield the two inseparable *title complex* diastereoisomers as a red oil (0.251 g, 95%, 1:3 d.r.), (Found: M<sup>+</sup>-2CO, 533.0044. C<sub>24</sub>H<sub>20</sub>O<sub>5</sub>CoMoN<sub>3</sub> requires M-2CO, 533.0047);  $\nu_{\max}$  (film)/cm<sup>-1</sup> 2047, 1994, 1935 (C≡O); Assigned from combined spectrum (i) Minor diastereoisomer  $\delta_H$  (250 MHz; CDCl<sub>3</sub>) 0.86 (3H, d, *J* 6.5 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 0.96 (3H, d, *J* 6.5 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.17-1.26 (2H, m, CHCH<sub>2</sub>), 1.70-1.89 (1H, m, CH(CH<sub>3</sub>)<sub>2</sub>), 2.81 (3H, s, CCH<sub>3</sub>), 5.21 (5H, s, CpH), 6.01 (1H, dd, *J* 3.2, 11.8 Hz, CCHCH<sub>2</sub>), 7.36-7.40 (2H, m,

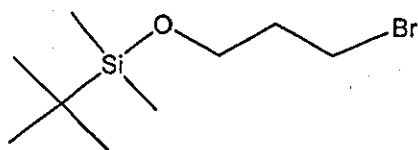
ArCH), 7.85-7.91 (2H, m, ArCH);  $\delta_c$  (100 MHz; CDCl<sub>3</sub>) 20.7, 21.7 (CH(CH<sub>3</sub>)<sub>2</sub>), 23.6 (CCH<sub>3</sub>), 25.4 (CH(CH<sub>3</sub>)<sub>2</sub>), 45.2 (CHCH<sub>2</sub>), 63.1 (CCHCH<sub>2</sub>), 89.5 (CH<sub>3</sub>C), 91.2 (CpC), 100.5 (CH<sub>3</sub>CC), 109.6, 120.3, 124.3, 127.5 (ArCH), 133.8, 146.0 (ArC), 203.5 (Co(CO)<sub>3</sub>), 223.9, 226.1 (MoCp(CO)<sub>2</sub>);  $m/z$  533 (M<sup>+</sup>-2CO, 16%), 505 (100), 477 (46).  
 (ii) Major diastereoisomer  $\delta_H$  (250 MHz; CDCl<sub>3</sub>) 0.84-0.94 (6H, m, CH(CH<sub>3</sub>)<sub>2</sub>), 1.17-1.26 (2H, m, CHCH<sub>2</sub>), 1.70-1.89 (1H, m, CH(CH<sub>3</sub>)<sub>2</sub>), 2.81 (3H, s, CCH<sub>3</sub>), 4.98 (5H, s, CpH), 5.82 (1H, dd,  $J$  3.0, 11.6 Hz, CCHCH<sub>2</sub>), 7.36-7.40 (2H, m, ArCH), 7.85-7.91 (2H, m, ArCH);  $\delta_c$  (100 MHz; CDCl<sub>3</sub>) 20.7, 21.7 (CH(CH<sub>3</sub>)<sub>2</sub>), 23.6 (CCH<sub>3</sub>), 25.4 (CH(CH<sub>3</sub>)<sub>2</sub>), 46.3 (CHCH<sub>2</sub>), 66.1 (CCHCH<sub>2</sub>), 89.5 (CH<sub>3</sub>C), 90.5 (CpC), 100.5 (CH<sub>3</sub>CC), 109.6, 120.3, 124.3, 127.5 (ArCH), 133.8, 146.0 (ArC), 203.5 (Co(CO)<sub>3</sub>), 224.4, 226.6 (MoCp(CO)<sub>2</sub>).

**2-(3-Bromopropoxy)tetrahydropyran<sup>118</sup>**



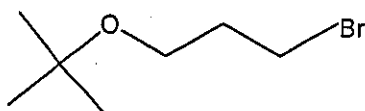
3,4-Dihydro-2H-pyran (0.39 mL, 4.30 mmol) was added to a dry RBF and dissolved in DCM (15 mL). *p*-Toluenesulfonic acid (one spatula measure) was added after heating to reflux followed by 3-bromo-1-propanol (0.33 mL, 3.60 mmol). The reaction mixture was stirred at reflux for 30 min and at ambient temperature for 1.0 h, before the addition of solid NaHCO<sub>3</sub> (two spatula measures) and filtration. The solvent was removed *in vacuo* to leave a yellow oil, which was purified by flash silica chromatography eluting in petroleum ether-diethyl ether (4:1 v/v) to yield the *title compound* as a clear oil (0.682 g, 85%);  $\nu_{\max}$  (film)/cm<sup>-1</sup> 2943 (sp<sup>3</sup> C-H), 1475, 1461 (C-O);  $\delta_H$  (250 MHz; CDCl<sub>3</sub>) 1.55-1.83 (6H, m, CH(CH<sub>2</sub>)<sub>3</sub>), 2.12 (2H, q,  $J$  6.2 Hz, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 3.48-3.56 (4H, m, BrCH<sub>2</sub>, OCH<sub>2</sub>), 3.83-3.92 (2H, m, CHOCH<sub>2</sub>), 4.61 (1H, s, OCHO);  $\delta_c$  (100 MHz; CDCl<sub>3</sub>) 19.5, 25.5, 30.6, 33.0, peak absent (CH<sub>2</sub>), 62.2, 64.9 (OCH<sub>2</sub>), 98.8 (CH).

(3-Bromopropoxy)-tert-butyldimethylsilane<sup>119</sup>



To a flame dried Schlenk flask was added *tert*-butyldimethylsilylchloride (1.300 g, 8.63 mmol) and *N,N*-dimethylaminopyridine (0.045 g, 0.29 mmol) which were dissolved in DCM (15 mL). After stirring for 15 min, triethylamine (1.20 mL, 8.63 mmol) and 3-bromopropanol (0.65 mL, 7.19 mmol) were added and the reaction mixture stirred for 24.0 h. The reaction mixture was then washed with saturated  $\text{NH}_4\text{Cl}$  (50 mL) solution and the product extracted into DCM, before drying over  $\text{Na}_2\text{SO}_4$ . The crude mixture was filtered and the solvent removed *in vacuo*, purifying the residue by flash silica chromatography eluting in petroleum ether-diethyl ether (6:1) to yield the *title compound* as a clear oil (1.520 g, 65%);  $\nu_{\text{max}}$  (film)/ $\text{cm}^{-1}$  2955, 2930, 2858 ( $\text{sp}^3$  C-H), 1472, 1464 (C-O);  $\delta_{\text{H}}$  (250 MHz;  $\text{CDCl}_3$ ) 0.07 (6H, s,  $\text{Si}(\text{CH}_3)_2$ ), 0.90 (9H, s,  $\text{C}(\text{CH}_3)_3$ ), 2.03 (2H, quint,  $J$  6.0 Hz,  $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 3.52 (2H, t,  $J$  8.0 Hz,  $\text{BrCH}_2$ ), 3.73 (2H, t,  $J$  5.5 Hz,  $\text{OCH}_2$ );  $\delta_{\text{C}}$  (100 MHz;  $\text{CDCl}_3$ ) -5.4 (2C, s,  $\text{Si}(\text{CH}_3)_2$ ), 18.3 ( $\text{SiC}(\text{CH}_3)_3$ ), 25.9 (3C, s,  $\text{C}(\text{CH}_3)_3$ ), 30.7 ( $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 35.6 ( $\text{CH}_2\text{Br}$ ), 60.4 ( $\text{OCH}_2$ ).

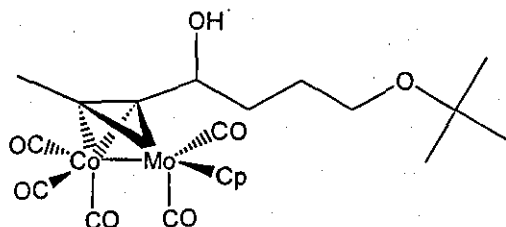
3-(*tert*-Butyloxy)-1-bromopropane (223)<sup>120</sup>



To a Schlenk flask containing a solution of 3-bromopropanol (3.080 g, 22.10 mmol) in *n*-hexane/DCM (5:1, 30 mL) and Amberlyst® 15 (0.550 g), fitted with a cold trap was added 2-methylpropene and the reaction mixture stirred for 24.0 h, following the reaction by TLC. Further additions of 2-methylpropene were carried out until no starting material was present. The crude mixture was then filtered through a pad of celite and silica. The solvent was removed *in vacuo* to leave a yellow oil, which was purified by flash silica chromatography eluting in petroleum ether-diethyl ether (10:1 v/v) to yield the *title compound* as a clear oil (3.540 g, 82%);  $\nu_{\text{max}}$  (film)/ $\text{cm}^{-1}$  2975,

2933 ( $sp^3$  C-H), 1478, 1390, 1363 (C-O);  $\delta_H$  (250 MHz;  $CDCl_3$ ) 1.20 (9H, s,  $C(CH_3)_3$ ), 2.05 (2H, q,  $J$  6.0 Hz,  $CH_2CH_2CH_2$ ), 3.46-3.55 (4H, m,  $BrCH_2$ ,  $OCH_2$ );  $\delta_C$  (100 MHz;  $CDCl_3$ ) 27.6 (3C, s,  $C(CH_3)_3$ ), 31.0 ( $CH_2CH_2CH_2$ ), 33.6 ( $CH_2Br$ ), 38.8 ( $OCH_2$ ), 72.6 ( $C(CH_3)_3$ ).

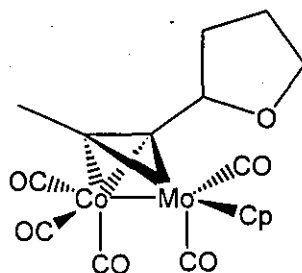
**Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-7-*tert*-butoxyhept-2-yn-4-ol (226)**



To magnesium turnings (0.025 g, 1.03 mmol) in dry THF (1 mL) was added 1,2-dibromoethane (0.04 mL, 0.47 mmol), followed by a solution of 3-(*tert*-butoxy)-1-bromopropane (0.240 g, 0.93 mmol) in dry THF (2 mL) and the reaction mixture was refluxed until no magnesium was present. After addition of dry THF (5 mL), the reaction mixture was cooled to  $-78^\circ C$  before cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-butynal (0.150 g, 0.35 mmol) in dry THF (3 mL) was added and the reaction mixture was left to stir for 1.5 h. The crude mixture was then filtered through a pad of celite and silica. The solvent was removed *in vacuo* to leave a red oil, which was purified by flash silica chromatography eluting in petroleum ether-diethyl ether (5:1 v/v) to yield the two inseparable *title complex* diastereoisomers as a red oil (0.159 g, 75%, 7:1 d.r.) (Found:  $M^+-3CO$ , 462.0144.  $C_{21}H_{25}O_7CoMo$  requires  $M-3CO$ , 462.0143);  $\nu_{max}$  (film)/ $cm^{-1}$  3378 (O-H), 2043, 1969, 1927 ( $C\equiv O$ ); Assigned from combined spectrum (i) Major diastereoisomer  $\delta_H$  (250 MHz;  $CDCl_3$ ) 1.21 (9H, s,  $C(CH_3)_3$ ), 1.43-1.57 (2H, m,  $CH_2CH_2CH_2$ ), 1.73-1.83 (2H, m,  $CHCH_2CH_2$ ), 2.70 (3H, s,  $CCH_3$ ), 3.30 (1H, d,  $J$  4.4 Hz,  $CHOH$ ), 3.34-3.50 (2H, m,  $OCH_2$ ), 4.50-4.55 (1H, m,  $CCHCH_2$ ), 5.45 (5H, s,  $CpH$ );  $\delta_C$  (100 MHz;  $CDCl_3$ ) 20.5 ( $CCH_3$ ), 27.3 (3C, s,  $C(CH_3)_3$ ), 27.4 ( $CH_2CH_2CH_2$ ), 37.7 ( $CHCH_2$ ), 61.5 ( $CH_2O$ ), 73.2 ( $C(CH_3)_3$ ), 75.4 ( $CH_2CH$ ), 90.2 ( $CpC$ ), 94.3 ( $CH_3C$ ), 97.8 ( $CH_3CC$ ), 204.4 ( $Co(CO)_3$ ), 224.8, 226.8 ( $MoCp(CO)_2$ );  $m/z$  462 ( $M^+-3CO$ , 100%), 445 (8), 406 (8). (ii) Minor diastereoisomer  $\delta_H$  (250 MHz;  $CDCl_3$ ) 1.20 (9H, s,  $C(CH_3)_3$ ), 1.43-1.84 (4H, m,  $CH_2CH_2CH_2$ ), 2.72

(3H, s, CCH<sub>3</sub>), 2.96 (1H, d, *J* 3.3 Hz, CHOH), 3.35-3.45 (2H, m, OCH<sub>2</sub>), 4.78-4.82 (1H, m, CCHCH<sub>2</sub>), 5.47 (5H, s, CpH);  $\delta_c$  (100 MHz; CDCl<sub>3</sub>) 20.5 (CCH<sub>3</sub>), 27.1 (3C, s, C(CH<sub>3</sub>)<sub>3</sub>), 27.5 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 36.5 (CHCH<sub>2</sub>), 61.4 (CH<sub>2</sub>O), 73.1 (C(CH<sub>3</sub>)<sub>3</sub>), 75.2 (CH<sub>2</sub>CH), 90.1 (CpC), 94.8 (CH<sub>3</sub>C), 98.3 (CH<sub>3</sub>CC), 204.4 (Co(CO)<sub>3</sub>), 225.1, 226.0 (MoCp(CO)<sub>2</sub>).

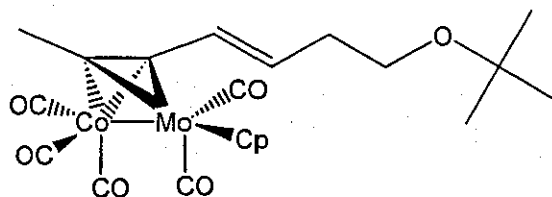
**Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-1-(tetrahydrofuran-2-yl)propyne (221)**



To a solution of cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-7-*tert*-butoxyhept-2-yn-4-ol (0.200 g, 0.37 mmol) under an atmosphere of nitrogen in dry DCM (15 mL) at -78°C, was added BF<sub>3</sub>·OEt<sub>2</sub> (0.14 mL, 1.11 mmol). The reaction mixture was stirred for 0.5 h and H<sub>2</sub>O (0.2 mL) was added before filtration through a pad of celite and silica, washing with DCM and ethanol. The solvent was removed *in vacuo* to leave a red oil, which was purified by flash silica chromatography eluting in petroleum ether-diethyl ether (10:1 v/v) to yield the two inseparable *title complex* diastereoisomers as a red oil (0.136 g, 79%, 2:1 d.r.) (Found: M<sup>+</sup>-CO, 443.9308. C<sub>17</sub>H<sub>15</sub>O<sub>6</sub>CoMo requires M-CO, 443.9306);  $\nu_{\max}$  (film)/cm<sup>-1</sup> 2044, 1969, 1926 (C≡O); Assigned from combined spectrum (i) Major diastereoisomer  $\delta_H$  (250 MHz; CDCl<sub>3</sub>) 1.57-1.71 (1H, m, CH<sub>2</sub>CHH), 1.87-2.02 (2H, m, CH<sub>2</sub>CH<sub>2</sub>), 2.11-2.24 (1H, m, CH<sub>2</sub>CHH), 2.68 (3H, s, CCH<sub>3</sub>), 3.76-3.94 (2H, m, CH<sub>2</sub>O), 4.83 (1H, t, *J* 6.9 Hz, CCHCH<sub>2</sub>), 5.44 (5H, s, CpH);  $\delta_c$  (100 MHz; CDCl<sub>3</sub>) 20.1 (CCH<sub>3</sub>), 26.7 (CHCH<sub>2</sub>), 34.0 (CH<sub>2</sub>CH<sub>2</sub>O), 67.9 (CH<sub>2</sub>O), 83.0 (CH<sub>2</sub>CH), 90.2 (CpC), 91.2 (CH<sub>3</sub>C), 98.4 (CH<sub>3</sub>CC), 204.4 (Co(CO)<sub>3</sub>), 224.9, 226.6 (MoCp(CO)<sub>2</sub>); *m/z* 472 (M<sup>+</sup>, 7%), 444 (14), 416 (100), 388 (67), 360 (34). (ii) Minor diastereoisomer  $\delta_H$  (250 MHz; CDCl<sub>3</sub>) 1.57-1.71 (1H, m, CH<sub>2</sub>CHH), 1.87-2.02 (2H, m, CH<sub>2</sub>CH<sub>2</sub>), 2.11-2.24 (1H, m, CH<sub>2</sub>CHH), 2.70 (3H, s, CCH<sub>3</sub>), 3.75-3.94 (2H, m, CH<sub>2</sub>O), 4.98 (1H, t, *J* 7.2 Hz, CCHCH<sub>2</sub>), 5.41 (5H, s, CpH);

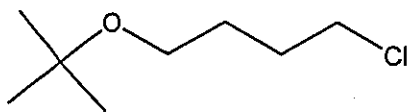
$\delta_c$  (100 MHz;  $CDCl_3$ ) 20.6 ( $CCH_3$ ), 26.6 ( $CHCH_2$ ), 33.2 ( $CH_2CH_2O$ ), 68.0 ( $CH_2O$ ), 83.1 ( $CH_2CH$ ), 90.2 ( $CpC$ ), 91.8 ( $CH_3C$ ), 98.5 ( $CH_3CC$ ), 204.4 ( $Co(CO)_3$ ), 225.2, 226.0 ( $MoCp(CO)_2$ ).

**Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-7-*tert*-butoxyhept-4-en-2-yne (227)**



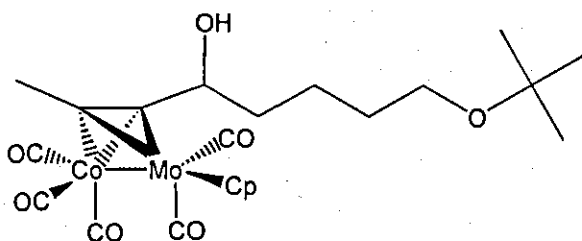
To a solution of cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-7-*tert*-butoxyhept-2-yn-4-ol (0.120 g, 0.22 mmol) under an atmosphere of nitrogen in dry DCM (15 mL) at  $-78^\circ C$ , was added TFA (0.03 mL, 0.33 mmol). The reaction mixture was stirred for 0.5 h and  $H_2O$  (0.2 mL) added before filtration through a pad of celite and silica, washing with DCM and ethanol. The solvent was removed *in vacuo* to leave a red oil, which was purified by flash silica chromatography eluting in petroleum ether-diethyl ether (10:1 v/v) to yield the *title complex* as a red oil (0.076 g, 70%) (Found:  $M^+-3CO$ , 444.0045.  $C_{21}H_{23}O_6CoMo$  requires  $M-3CO$ , 444.0038);  $\nu_{max}$  (film)/ $cm^{-1}$  2045, 1976, 1933 ( $C\equiv O$ );  $\delta_H$  (250 MHz;  $CDCl_3$ ) 1.19 (9H, s,  $C(CH_3)_3$ ), 2.36 (2H, q,  $J$  6.5 Hz,  $CHCH_2CH_2$ ), 2.65 (3H, s,  $CCH_3$ ), 3.40 (2H, t,  $J$  6.5 Hz,  $CH_2O$ ), 5.33 (5H, s,  $CpH$ ), 5.66-5.77 (1H, m,  $CHCH_2$ ), 6.47 (1H, d,  $J$  15.0 Hz,  $CCHCH$ );  $\delta_c$  (100 MHz;  $CDCl_3$ ) 21.1 ( $CCH_3$ ), 27.6 (3C, s,  $C(CH_3)_3$ ), 34.1 ( $CHCH_2$ ), 61.4 ( $CH_2O$ ), 72.7 ( $C(CH_3)_3$ ), 88.9 ( $CH_3C$ ), 91.1 ( $CpC$ ), 95.0 ( $CH_3CC$ ), 130.9 ( $CHCH_2$ ), 131.3 ( $CCH$ ), 203.6 ( $Co(CO)_3$ ), 225.2, 226.3 ( $MoCp(CO)_2$ );  $m/z$  444 ( $M^+-3CO$ , 100%), 416 (62), 388 (21).

4-(*tert*-Butyloxy)-1-chlorobutane (224)<sup>120</sup>



To a Schlenk flask containing a solution of 4-chlorobutanol (2.35 g, 18.40 mmol) in *n*-hexane/DCM (5:1, 30 mL) and Amberlyst® 15 (0.500 g), fitted with a cold trap was added 2-methylpropene and the reaction mixture stirred for 24.0 h, following the reaction by TLC. Further additions of 2-methylpropene were carried out until no starting material was present. The crude mixture was then filtered through a pad of celite and silica. The solvent was removed *in vacuo* to leave a yellow oil, which was purified by flash silica chromatography eluting in petroleum ether-diethyl ether (10:1 v/v) to yield the *title compound* as a clear oil (2.48 g, 82%);  $\nu_{\max}$  (film)/cm<sup>-1</sup> 2973, 2937 (sp<sup>3</sup> C-H), 1391, 1362 (C-O), 731 (C-Cl);  $\delta_{\text{H}}$  (250 MHz; CDCl<sub>3</sub>) 1.18 (9H, s, C(CH<sub>3</sub>)<sub>3</sub>), 1.62-1.69 (2H, m, CH<sub>2</sub>CH<sub>2</sub>Cl), 1.82-1.89 (2H, m, OCH<sub>2</sub>CH<sub>2</sub>), 3.37 (2H, t, *J* 6.2 Hz, ClCH<sub>2</sub>), 3.57 (2H, t, *J* 6.8 Hz, OCH<sub>2</sub>);  $\delta_{\text{C}}$  (100 MHz; CDCl<sub>3</sub>) 27.6 (3C, s, C(CH<sub>3</sub>)<sub>3</sub>), 28.0 (CH<sub>2</sub>CH<sub>2</sub>Cl), 29.8 (CH<sub>2</sub>CH<sub>2</sub>O), 45.1 (ClCH<sub>2</sub>), 60.6 (OCH<sub>2</sub>), 72.6 (C(CH<sub>3</sub>)<sub>3</sub>).

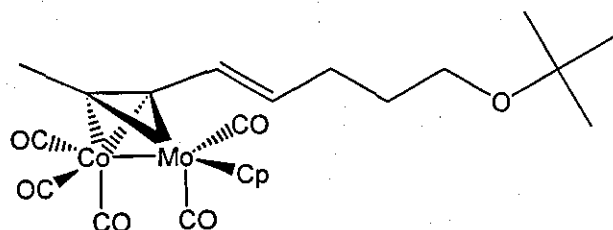
Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-8-*tert*-butoxyoct-2-yn-4-ol



To magnesium turnings (0.035 g, 1.43 mmol) in dry THF (1 mL) was added 1,2-dibromoethane (0.03 mL, 0.36 mmol), followed by a solution of 3-*tert*-butoxy-1-bromopropane (0.231 g, 1.30 mmol) in dry THF (2 mL) and the reaction mixture was refluxed until no magnesium was present. After addition of dry THF (5 mL), the reaction mixture was cooled to -78°C before cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-butyne (0.185 g, 0.43 mmol) in dry THF (3 mL) was added and the reaction mixture was left to stir for 1.5 h. The reaction mixture was then filtered

through a pad of celite and silica. The solvent was removed *in vacuo* to leave a red oil, which was purified by flash silica chromatography eluting in petroleum ether-diethyl ether (5:1 v/v) to yield the two inseparable *title complex* diastereoisomers as a red oil (0.178 g, 74%, 3:1 d.r.) (Found:  $M^+-3CO$ , 476.0305.  $C_{22}H_{27}O_7CoMo$  requires  $M-3CO$ , 476.0295);  $\nu_{max}$  (film)/ $cm^{-1}$  3425 (O-H), 2042, 1967, 1928 ( $C\equiv O$ ); Assigned from combined spectrum (i) Major diastereoisomer  $\delta_H$  (250 MHz;  $CDCl_3$ ) 1.18 (9H, s,  $C(CH_3)_3$ ), 1.43-1.85 (6H, m,  $CH(CH_2)_3CH_2$ ), 2.69 (3H, s,  $CCH_3$ ), 3.35 (2H, m,  $OCH_2$ ), 4.50 (1H, m,  $CCHCH_2$ ), 5.43 (5H, s,  $CpH$ );  $\delta_c$  (100 MHz;  $CDCl_3$ ) 20.9 ( $CCH_3$ ), 23.8 ( $CHCH_2CH_2$ ), 27.9 (3C, s,  $C(CH_3)_3$ ), 30.6 ( $OCH_2CH_2$ ), 40.1 ( $CHCH_2$ ), 61.7 ( $CH_2O$ ), 73.0 ( $C(CH_3)_3$ ), 75.9 ( $CH_2CH$ ), 90.5 ( $CpC$ ), 94.4 ( $CH_3C$ ), 98.0 ( $CH_3CC$ ), peak absent ( $Co(CO)_3$ ), 224.9, 226.8 ( $MoCp(CO)_2$ );  $m/z$  476 ( $M^+-3CO$ , 100%), 459 (7), 420 (10). (ii) Minor diastereoisomer  $\delta_H$  (250 MHz;  $CDCl_3$ ) 1.18 (9H, s,  $C(CH_3)_3$ ), 1.43-1.85 (6H, m,  $CH(CH_2)_3CH_2$ ), 2.71 (3H, s,  $CCH_3$ ), 3.35 (2H, m,  $OCH_2$ ), 4.79 (1H, m,  $CCHCH_2$ ), 5.47 (5H, s,  $CpH$ );  $\delta_c$  (100 MHz;  $CDCl_3$ ) 20.9 ( $CCH_3$ ), 23.8 ( $CH_2$ ), 27.9 (3C, s,  $C(CH_3)_3$ ), 30.6 ( $CH_2$ ), 40.1 ( $CHCH_2$ ), 61.7 ( $CH_2O$ ), 73.0 ( $C(CH_3)_3$ ), 75.5 ( $CH_2CH$ ), 90.4 ( $CpC$ ), 94.4 ( $CH_3C$ ), 98.0 ( $CH_3CC$ ), peak absent ( $Co(CO)_3$ ), 224.9, 226.8 ( $MoCp(CO)_2$ ).

**Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-8-*tert*-butoxyoct-4-en-2-yne**

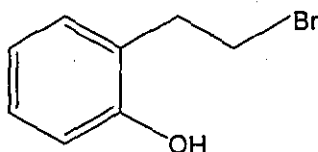


To a solution of cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-7-*tert*-butoxyhept-2-yn-4-ol (0.175 g, 0.31 mmol) under an atmosphere of nitrogen in dry acetonitrile (15 mL) at  $-40^\circ C$ , was added  $BF_3 \cdot OEt_2$  (0.12 mL, 0.94 mmol). The reaction mixture was stirred for 0.5 h before filtration through a pad of celite and silica, washing with DCM and ethanol. The solvent was removed *in vacuo* to leave a red oil, which was purified by flash silica chromatography eluting in petroleum ether-diethyl ether (10:1 v/v) to yield the *title complex* as a red oil (0.083 g, 49%) (Found:  $M^+$ , 542.0035.



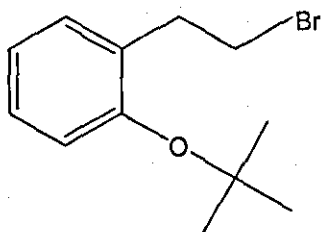
$C_{22}H_{25}O_6CoMo$  requires M, 542.0042);  $\nu_{max}$  (film)/ $cm^{-1}$  2044, 1975, 1932 (C $\equiv$ O);  $\delta_H$  (250 MHz;  $CDCl_3$ ) 1.18 (9H, s, C(CH $_3$ ) $_3$ ), 1.65 (2H, q,  $J$  6.9 Hz, CH $_2$ CH $_2$ CH $_2$ ), 2.24 (2H, q,  $J$  6.9 Hz, CHCH $_2$ CH $_2$ ), 2.64 (3H, s, CCH $_3$ ), 3.36 (2H, t,  $J$  6.5 Hz, CH $_2$ O), 5.33 (5H, s, CpH), 5.65-5.77 (1H, m, CHCH $_2$ ), 6.42 (1H, d,  $J$  15.0 Hz, CCHCH);  $\delta_c$  (100 MHz;  $CDCl_3$ ) 21.6 (CCH $_3$ ), 27.9 (3C, s, C(CH $_3$ ) $_3$ ), 29.8 (CH $_2$ CH $_2$ CH $_2$ ), 30.7 (CHCH $_2$ ), 60.9 (CH $_2$ O), 72.9 (C(CH $_3$ ) $_3$ ), 89.5 (CH $_3$ C), 91.3 (CpC), 95.0 (CH $_3$ CC), 130.1 (CHCH $_2$ ), 134.5 (CCH), 204.0 (Co(CO) $_3$ ), 225.6, 226.6 (MoCp(CO) $_2$ );  $m/z$  542 ( $M^+$ , 4%), 514 (10), 458 (100), 430 (25), 402 (8).

### 2-(2-Hydroxyphenyl)bromoethane



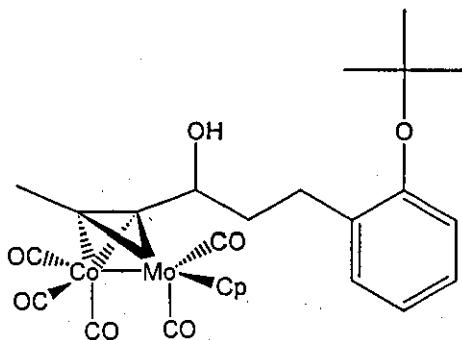
To a Schlenk flask containing  $PBr_3$  (0.18 mL, 1.88 mmol) was added HBr in acetic acid (3 drops) at 0°C and the mixture stirred for 5 min. 2-(2-Hydroxyphenyl)ethanol (0.500 g, 3.62 mmol) was added over 1.0 h at 0-10°C and the reaction mixture stirred for 2.0 d. Ice-water (20 mL) was added and the crude product extracted into DCM (3 x 15 mL). The extracts were washed with a saturated  $NaHCO_3$  solution (15 mL) and dried over solid  $MgSO_4$ . The solvent was removed *in vacuo* to leave a yellow oil, which was purified by flash silica chromatography eluting in petroleum ether-diethyl ether (2:1 v/v) to yield the *title compound* as a yellow oil (0.350 g, 49%) (Found:  $M^+$ , 199.9837.  $C_8H_9^{79}BrO$  requires M, 199.9837);  $\nu_{max}$  (film)/ $cm^{-1}$  3510 (O-H), 2965 ( $sp^3$  C-H), 1457 (C-O);  $\delta_H$  (250 MHz;  $CDCl_3$ ) 3.19 (2H, t,  $J$  7.6 Hz, ArCH $_2$ ), 3.62 (2H, t,  $J$  7.6 Hz, CH $_2$ Br), 6.73-6.76 (1H, m, ArCH), 6.87-6.92 (1H, m, ArCH), 7.11-7.16 (2H, m, ArCH);  $\delta_c$  (100 MHz;  $CDCl_3$ ) 32.6 (ArCH $_2$ ), 34.7 (CH $_2$ Br), 115.9, 121.4, (ArCH), 125.8 (ArC), 128.7, 131.5 (ArCH), 154.0 (ArCO);  $m/z$  202 ( $M^+$  ( $^{81}Br$ ), 28%) 200 (28), 121 (27), 107 (100), 91 (25), 77 (21).

2-(2-*tert*-Butoxyphenyl)bromoethane (222)



To a Schlenk flask containing a solution of 2-(2-hydroxyphenyl)bromoethane (0.350 g, 1.74 mmol) in *n*-hexane/DCM (5:1 v/v, 12 mL) and Amberlyst® 15 (0.150 g), fitted with a cold trap was added 2-methylpropene and the reaction mixture was stirred for 24.0 h, following the reaction by TLC. Further additions of 2-methylpropene were carried out until no starting material was present. The reaction mixture was then filtered through a pad of celite and silica. The solvent was removed *in vacuo* to leave a yellow oil, which was purified by flash silica chromatography eluting in petroleum ether-diethyl ether (10:1 v/v) to yield the *title compound* as a clear oil (0.240 g, 54%) (Found:  $M^+$ , 256.0437.  $C_{12}H_{17}^{79}BrO$  requires  $M$ , 256.0443);  $\nu_{\max}$  (film)/ $\text{cm}^{-1}$  2974 ( $\text{sp}^3$  C-H), 1486, 1336 (C-O);  $\delta_{\text{H}}$  (250 MHz;  $\text{CDCl}_3$ ) 1.43 (9H, s,  $\text{C}(\text{CH}_3)_3$ ), 3.16 (2H, t,  $J$  7.9 Hz,  $\text{ArCH}_2$ ), 3.56 (2H, t,  $J$  7.9 Hz,  $\text{CH}_2\text{Br}$ ), 6.91-6.97 (1H, m,  $\text{ArCH}$ ), 7.03-7.06 (1H, m,  $\text{ArCH}$ ), 7.13-7.18 (2H, m,  $\text{ArCH}$ );  $\delta_{\text{C}}$  (100 MHz;  $\text{CDCl}_3$ ) 28.3 (3C, s,  $\text{C}(\text{CH}_3)_3$ ), 30.8 ( $\text{ArCH}_2$ ), 34.5 ( $\text{CH}_2\text{Br}$ ), 77.8 ( $\text{C}(\text{CH}_3)_3$ ), 119.5, 121.0, 126.5, 129.4 ( $\text{ArCH}$ ), 130.7 ( $\text{ArC}$ ), 153.5 ( $\text{ArCO}$ );  $m/z$  258 ( $M^+$  ( $^{81}\text{Br}$ ), 3%), 256 (4), 243 (10), 241 (10), 202 (53), 200 (55), 161 (5), 121 (39), 107 (100).

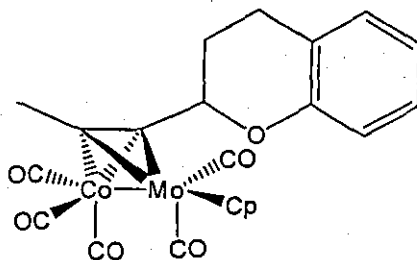
**Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-6-(2-*tert*-  
butoxyphenyl)hex-2-yn-4-ol (229)**



To magnesium turnings (0.025 g, 1.03 mmol) in dry THF (1 mL) was added 1,2-dibromoethane (0.04 mL, 0.47 mmol), followed by a solution of *tert*-butoxy-1-bromopropane (0.240 g, 0.93 mmol) in dry THF (2 mL) and the reaction mixture was refluxed until no magnesium was present. After addition of dry THF (5 mL), the reaction mixture was cooled to  $-78^{\circ}\text{C}$  before cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-butynal (0.150 g, 0.35 mmol) in dry THF (3 mL) was added and the reaction mixture was left to stir for 1.5 h. The reaction mixture was then filtered through a pad of celite and silica. The solvent was removed *in vacuo* to leave a red oil, which was purified by flash silica chromatography eluting in petroleum ether-diethyl ether (5:1 v/v) to yield the two inseparable *title complex* diastereoisomers as a red oil (0.159 g, 75%, 7:1 d.r.) (Found:  $\text{M}^+\text{-CO}$ , 580.0197.  $\text{C}_{26}\text{H}_{27}\text{O}_7\text{CoMo}$  requires  $\text{M-CO}$ , 580.0194);  $\nu_{\text{max}}$  (film)/ $\text{cm}^{-1}$  3462 (O-H), 2042, 1968, 1928 ( $\text{C}\equiv\text{O}$ ); Assigned from combined spectrum (i) Major diastereoisomer  $\delta_{\text{H}}$  (400 MHz;  $\text{CDCl}_3$ ) 1.44 (9H, s,  $\text{C}(\text{CH}_3)_3$ ), 1.73-1.85 (1H, m,  $\text{CH}_2\text{CHHCH}$ ), 1.92-2.00 (1H, m,  $\text{CH}_2\text{CHHCH}$ ), 2.21 (1H, d,  $J$  4.8 Hz,  $\text{CHOH}$ ), 2.68 (3H, s,  $\text{CCH}_3$ ), 2.88 (2H, t,  $J$  7.4 Hz,  $\text{ArCH}_2$ ), 4.40 (1H, d,  $J$  9.6 Hz,  $\text{CCHCH}_2$ ), 5.39 (5H, s,  $\text{CpH}$ ), 6.97-7.23 (4H, m,  $\text{ArCH}$ );  $\delta_{\text{C}}$  (100 MHz;  $\text{CDCl}_3$ ) 20.9 ( $\text{CCH}_3$ ), 28.4 ( $\text{CHCH}_2$ ), 29.6 (3C, s,  $\text{C}(\text{CH}_3)_3$ ), 40.5 ( $\text{ArCH}_2$ ), 75.2 ( $\text{CH}_2\text{CH}$ ), 79.6 ( $\text{C}(\text{CH}_3)_3$ ), 90.6 ( $\text{CpC}$ ), 94.0 ( $\text{CH}_3\text{C}$ ), 98.0 ( $\text{CH}_3\text{CC}$ ), 121.7, 123.1, 127.0, 130.5 ( $\text{ArCH}$ ), 135.2, 154.6 ( $\text{ArC}$ ), 204.6 ( $\text{Co}(\text{CO})_3$ ), 225.1, 226.9 ( $\text{MoCp}(\text{CO})_2$ );  $m/z$  608 ( $\text{M}^+$ , 2%), 580 (24), 524 (100). (ii) Minor diastereoisomer  $\delta_{\text{H}}$  (400 MHz;  $\text{CDCl}_3$ ) 1.44 (9H, s,  $\text{C}(\text{CH}_3)_3$ ), 1.73-1.85 (1H, m,  $\text{CH}_2\text{CHHCH}$ ), 1.92-2.00 (1H, m,  $\text{CH}_2\text{CHHCH}$ ), 2.20-2.22 (1H, m,  $\text{CHOH}$ ), 2.68 (3H, s,  $\text{CCH}_3$ ), 2.83-2.90 (2H, m,  $\text{ArCH}_2$ ), 4.67-4.70 (1H, d,  $J$  9.6 Hz,  $\text{CCHCH}_2$ ), 5.37 (5H, s,  $\text{CpH}$ ), 6.97-7.23 (4H, m,  $\text{ArCH}$ );  $\delta_{\text{C}}$  (100

MHz; CDCl<sub>3</sub>) 20.7 (CCH<sub>3</sub>), 28.1 (CHCH<sub>2</sub>), 29.6 (3C, s, C(CH<sub>3</sub>)<sub>3</sub>), 39.7 (ArCH<sub>2</sub>), 75.0 (CH<sub>2</sub>CH), 79.5 (C(CH<sub>3</sub>)<sub>3</sub>), 90.5 (CpC), 94.0 (CH<sub>3</sub>C), 98.0 (CH<sub>3</sub>CC), 121.6, 123.0, 126.6, 130.4 (ArCH), 135.2, 154.5 (ArC), 204.6 (Co(CO)<sub>3</sub>), 225.4, 226.2 (MoCp(CO)<sub>2</sub>).

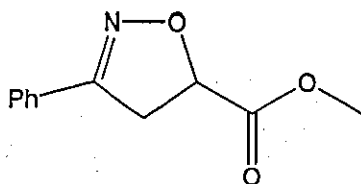
**Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-1-(1,2,3,4-tetrahydrobenzo[b]pyran-2-yl)propyne (230)**



To a solution of cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-6-(2-*tert*-butoxyphenyl)hex-2-yn-4-ol (0.140 g, 0.23 mmol) under an atmosphere of nitrogen in dry DCM (15 mL) at -78°C, was added BF<sub>3</sub>·OEt<sub>2</sub> (0.09 mL, 0.69 mmol). The reaction mixture was stirred for 0.5 h and H<sub>2</sub>O (0.2 mL) was added before filtration through a pad of celite and silica, washing with DCM and ethanol. The solvent was removed *in vacuo* to leave a red oil, which was purified by flash silica chromatography eluting in petroleum ether-diethyl ether (10:1 v/v) to yield the two inseparable *title complex* diastereoisomers as a red oil (0.023 g, 20%, 2:1 d.r.) (Found: M<sup>+</sup>-CO, 505.9462. C<sub>22</sub>H<sub>17</sub>O<sub>6</sub>CoMo requires M-CO, 505.9453);  $\nu_{\max}$  (film)/cm<sup>-1</sup> 2045, 1972, 1929 (C≡O); Assigned from combined spectrum (i) Major diastereoisomer  $\delta_{\text{H}}$  (400 MHz; CDCl<sub>3</sub>) 1.74-1.86 (1H, m, CHHCH), 2.05-2.17 (1H, m, CHHCH), 2.76 (3H, s, CCH<sub>3</sub>), 2.65-2.80 (1H, m, ArCHH), 2.94-3.02 (1H, m, ArCHH), 5.13 (1H, d, *J* 10.4 Hz, CCHCH<sub>2</sub>), 5.46 (5H, s, CpH), 6.79-6.86 (2H, m, ArCH), 7.05-7.14 (2H, m, ArCH);  $\delta_{\text{C}}$  (100 MHz; CDCl<sub>3</sub>) 20.6 (CCH<sub>3</sub>), 25.7 (CHCH<sub>2</sub>), 30.0 (ArCH<sub>2</sub>), 80.5 (CCH), 90.4 (CpC), 90.8 (CH<sub>3</sub>C), 91.4 (CH<sub>3</sub>CC), 117.0, 120.6, (ArCH), 122.1 (ArC), 127.7, 129.8 (ArCH), 155.4, peak absent (Co(CO)<sub>3</sub>), 224.9, 225.3, 226.0 (MoCp(CO)<sub>2</sub>); *m/z* 534 (M<sup>+</sup>, 5%), 506 (18), 450 (80), 422 (15). (ii) Minor diastereoisomer  $\delta_{\text{H}}$  (400 MHz; CDCl<sub>3</sub>) 1.74-1.86 (1H, m, CHHCH), 2.05-2.17 (1H, m, CHHCH), 2.70 (3H, s, CCH<sub>3</sub>), 2.65-2.80 (1H, m, ArCHH), 2.94-3.02 (1H, m, ArCHH), 4.90-4.93 (1H, d, *J* 10.4 Hz, CCHCH<sub>2</sub>),

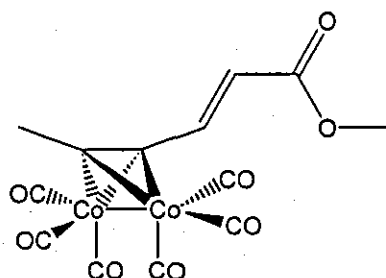
5.50 (5H, s, CpH), 6.79-6.86 (2H, m, ArCH), 7.05-7.14 (2H, m, ArCH);  $\delta_c$  (100 MHz; CDCl<sub>3</sub>) 20.7 (CCH<sub>3</sub>), 25.9 (CHCH<sub>2</sub>), 29.7 (ArCH<sub>2</sub>), 80.4 (CCH), 90.6 (CpC), 90.8 (CH<sub>3</sub>C), 91.4 (CH<sub>3</sub>CC), 116.9, 120.6, (ArCH), 122.2 (ArC), 127.7, 129.9 (ArCH), 155.4 (ArC), peak absent (Co(CO)<sub>3</sub>), 224.9, 225.3, 226.0 (MoCp(CO)<sub>2</sub>).

**Methyl-3-phenyl-4,5-dihydroisoxazole-5-carboxylate (238)**<sup>121</sup>



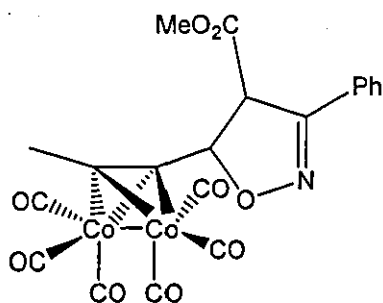
To benzaldehyde oxime (0.170 g, 1.40 mmol) in CHCl<sub>3</sub> (3 mL) was added *N*-chlorosuccinimide (0.207 g, 1.55 mmol) in CHCl<sub>3</sub> (10 mL) in a 2-neck flame-dried flask under an atmosphere of nitrogen. The reaction mixture was refluxed for 0.5 h at 75°C, with a colour change generally of pale yellow to a very pale sky blue. After cooling to room temperature methyl acrylate (0.133 g, 1.55 mmol) in CHCl<sub>3</sub> (3 mL) was added, followed by triethylamine (0.157 g, 1.55 mmol) in CHCl<sub>3</sub> (3 mL) over 0.5 h. The reaction mixture was heated under reflux for 2.0 h, producing a deep yellow/orange colour, then left to stir for 17.0 h at ambient temperature. The mixture product was concentrated *in vacuo* and the crude product purified by flash silica chromatography eluting in petroleum ether-diethyl ether (4:1 v/v), then recrystallised in diethyl ether-*n*-hexane to yield the *title compound* as pale yellow crystals (0.125 g, 45%), mp 71-72°C (lit., 72-73°C);  $\delta_H$  (250 MHz; CDCl<sub>3</sub>) 3.63 (1H, d, *J* 2.8 Hz, CH<sub>2</sub>), 3.81 (3H, s, CH<sub>3</sub>), 5.17-5.20 (1H, m, OCH), 7.39-7.42 (3H, m, ArCH), 7.65-7.69 (2H, m, ArCH);  $\delta_c$  (100 MHz; CD<sub>2</sub>Cl<sub>2</sub>) 26.5 (CH<sub>3</sub>), 47.6 (CH<sub>2</sub>), 72.2 (CCH), 78.1 (OCC), 125.8 (2C, s, ArCH), 128.0 (2C, s, ArCH), 128.7 (ArC), 129.5 (ArCH), 155.5 (NCCH<sub>2</sub>), 178.1 (CO<sub>2</sub>CH<sub>3</sub>).

**Dicobalt hexacarbonyl-methyl-(E)-hex-2-en-4-ynoate (240)<sup>122</sup>**



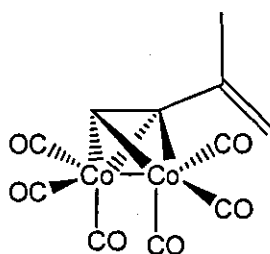
To water (100 mL) was added methoxycarbonylmethyltriphenylphosphonium bromide (1.530 g, 4.27 mmol) and the mixture stirred until the solid dissolved. To this was added NaOH (2 pellets) and the solution stirred to form a white precipitate in suspension. This was extracted with DCM (3 x 30 mL), and the extracts dried over MgSO<sub>4</sub>, filtered and concentrated *in vacuo* to yield an off-white solid. This was taken up in dry THF (2 x 20 mL), added to a flame-dried 3-neck flask containing dicobalt hexacarbonyl-2-butyne (1.080 g, 3.07 mmol) in dry THF (10 mL) under an atmosphere of nitrogen, then stirring for 20.0 h. The reaction mixture was then filtered through a plug of celite and concentrated *in vacuo*. The crude product was purified by flash silica column chromatography eluting with petroleum ether-diethyl ether (20:1 v/v) to yield the *title complex* as a deep red oil (1.240 g, 91%) (Found:  $M^+$ , 409.8882. C<sub>13</sub>H<sub>8</sub>O<sub>8</sub>Co<sub>2</sub> requires  $M$ , 409.8883);  $\nu_{\max}$  (film)/cm<sup>-1</sup> 2094, 2053, 2021 (C≡O), 1719, 1636 (C=O);  $\delta_H$  (250 MHz; CDCl<sub>3</sub>) 2.70 (3H, s, CCH<sub>3</sub>), 3.79 (3H, s, CO<sub>2</sub>CH<sub>3</sub>), 6.16 (1H, d,  $J$  15.0 Hz, CCHCH), 7.88 (1H, d,  $J$  15.0 Hz, CHCHCO<sub>2</sub>CH<sub>3</sub>);  $\delta_C$  (100 MHz; CDCl<sub>3</sub>) 20.9 (CCH<sub>3</sub>), 52.1 (CO<sub>2</sub>CH<sub>3</sub>), 86.7 (CCH<sub>3</sub>), 97.5 (CCHCH), 122.9 (CCHCH), 144.5 (CCHCH), 167.1 (CO<sub>2</sub>CH<sub>3</sub>), 197.0, 199.9 (Co(CO)<sub>3</sub>);  $m/z$  410 ( $M^+$ , 21%), 382 (54), 354 (71), 326 (100).

**Dicobalt hexacarbonyl-methyl-3-phenyl-5-propynyl-4,5-dihydroisoxazole-4-carboxylate (241)**



To benzaldehyde oxime (0.094 g, 0.80 mmol) in  $\text{CHCl}_3$  (1 mL) was added *N*-chlorosuccinimide (0.104 g, 0.80 mmol) in  $\text{CHCl}_3$  (3 mL) in a 2-neck flame-dried flask under an atmosphere of nitrogen. The reaction mixture was refluxed for 1.0 h at  $75^\circ\text{C}$ , with a colour change generally of pale yellow to a very pale sky blue. After cooling to room temperature dicobalt hexacarbonyl-methyl-(*E*)-hex-2-en-4-ynoate (0.106 g, 0.30 mmol) in  $\text{CHCl}_3$  (2 x 1 mL) was added, followed by triethylamine (0.079 g, 0.80 mmol) in  $\text{CHCl}_3$  (3 mL) over 0.5 h, evacuating the evolving HCl gas with nitrogen gas. The reaction mixture was then left to stir for 24.0 h. The crude product was concentrated *in vacuo* and purified by flash silica chromatography eluting in petroleum ether-diethyl ether (5:1 v/v) to yield the *title complex* as a deep red/orange oil (0.078 g, 57%);  $\nu_{\text{max}}$  (film)/ $\text{cm}^{-1}$  2094, 2054, 2022 ( $\text{C}\equiv\text{O}$ ), 1742 ( $\text{C}=\text{O}$ );  $\delta_{\text{H}}$  (250 MHz;  $\text{CDCl}_3$ ) 2.70 (3H, s,  $\text{CH}_3$ ), 3.77 (3H, s,  $\text{CH}_3\text{CO}_2$ ), 4.38 (1H, d, *J* 5.3 Hz, CCH), 6.11 (1H, d, *J* 5.3 Hz, OCH), 7.40-7.43 (3H, m, ArCH), 7.71-7.74 (2H, m, ArCH);  $\delta_{\text{C}}$  (100 MHz;  $\text{CDCl}_3$ ) 20.7 ( $\text{CCH}_3$ ), 53.6 ( $\text{CO}_2\text{CH}_3$ ), 61.1 ( $\text{CHCO}_2\text{CH}_3$ ), 86.1 ( $\text{CCHO}$ ), 93.1 ( $\text{CCH}_3$ ), 95.4 ( $\text{CHCC}$ ), 127.4, 128.7, 129.3 (ArCH), 130.9 (ArC), 154.1 ( $\text{CO}_2\text{CH}_3$ ), 169.4 ( $\text{NCCH}_2$ ), peak absent ( $\text{Co}(\text{CO})_3$ ); *m/z* 473 ( $\text{M}^+ - 2\text{CO}$ , 53%), 445 (22), 417 (35), 389 (67), 361 (100).

Dicobalt hexacarbonyl-2-methylbut-1-enyne (243)<sup>97</sup>

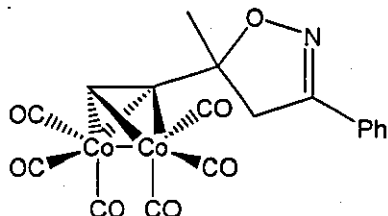


To a flame-dried 3-neck flask under an atmosphere of nitrogen was added dicobalt octacarbonyl (2.030 g, 5.94 mmol) and DCM (20 mL). 2,2-Dimethyl-3-butyne-2-ol (0.500 g, 5.94 mmol) in DCM (5 mL) was added and the mixture left to stir under an atmosphere of nitrogen for 2.0 h at ambient temperature. Then *p*-toluenesulfonic acid (a spatula measure) was added and the reaction mixture was left to stir for 24.0 h, adding two more portions of *p*-toluenesulfonic acid. Solid NaHCO<sub>3</sub> (two spatula measures) was then added and the reaction mixture was filtered through a plug of celite, concentrated *in vacuo* and the residue purified by flash silica chromatography eluting in petroleum ether-diethyl ether (15:1 v/v), to yield the *title complex* as a deep red oil (1.570 g, 75%) (Found:  $M^+$ , 351.8835. C<sub>11</sub>H<sub>6</sub>O<sub>6</sub>Co<sub>2</sub> requires  $M$ , 351.8828);  $\nu_{\max}$  (film)/cm<sup>-1</sup> 2094, 2053, 2022 (C≡O);  $\delta_H$  (250 MHz; CDCl<sub>3</sub>) 2.08 (3H, s, CCH<sub>3</sub>), 5.27 (1H, t,  $J$  1.5 Hz, CCHH), 5.40 (1H, q,  $J$  0.8 Hz, CCHH), 6.19 (1H, s, CCH);  $\delta_c$  (100 MHz; CDCl<sub>3</sub>) 24.5 (CCH<sub>3</sub>), 91.4 (CHCC), 93.2 (CHCC), 118.1 (CCH<sub>2</sub>), 141.5 (CHCC), 199.6, 199.7, 199.9, 200.0, 200.2 (Co(CO)<sub>3</sub>);  $m/z$  352 ( $M^+$ , 10%), 324 (18), 296 (19), 268 (13).

Dicobalt hexacarbonyl 2,2-dimethyl-3-butyne-2-ol<sup>97</sup> was also isolated as a deep red oil (0.600 g, 20%) (Found:  $M^+$ , 369.8928. C<sub>11</sub>H<sub>8</sub>O<sub>7</sub>Co<sub>2</sub> requires  $M$ , 369.8934);  $\nu_{\max}$  (film)/cm<sup>-1</sup> 2094, 2053, 2022 (C≡O);  $\delta_H$  (250 MHz; CDCl<sub>3</sub>) 1.57 (6H, s, C(CH<sub>3</sub>)<sub>2</sub>), 6.02 (1H, s, CCH);  $\delta_c$  (100 MHz; CDCl<sub>3</sub>) 33.2 (2C, s, C(CH<sub>3</sub>)<sub>2</sub>), 71.6 (CHCC), 72.7 (CCH), 106.0 (CCOH), 199.7 (Co(CO)<sub>3</sub>);  $m/z$  370 ( $M^+$ , 12%), 342 (87), 314 (100), 286 (100).

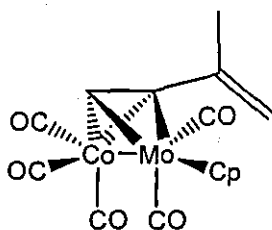


**Dicobalt hexacarbonyl-5-ethynyl-5-methyl-3-phenyl-4,5-dihydroisoxazole (244)**<sup>97</sup>



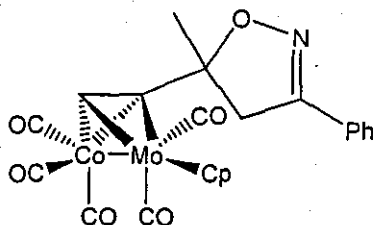
To benzaldehyde oxime (0.310 g, 2.56 mmol) in  $\text{CHCl}_3$  (2 mL) was added *N*-chlorosuccinimide (0.341 g, 2.56 mmol) in  $\text{CHCl}_3$  (6 mL) in a 2-neck flame-dried flask under an atmosphere of nitrogen. The reaction mixture was then refluxed for 1.0 h at  $75^\circ\text{C}$ , with a colour change generally of pale yellow to a very pale sky blue. After cooling to room temperature dicobalt hexacarbonyl-2-methylbut-1-enyne (0.300 g, 0.85 mmol) in  $\text{CHCl}_3$  (2 x 1.5 mL) was added, followed by triethylamine (0.259 g, 2.56 mmol) in  $\text{CHCl}_3$  (5 mL) over 1.0 h, evacuating the evolving HCl gas with nitrogen gas. The reaction mixture was left to stir for 24.0 h. The crude product mixture was then concentrated *in vacuo* and the crude product purified by flash silica chromatography eluting in petroleum ether-diethyl ether (15:1 v/v) to yield the *title complex* as a deep red oil (0.367 g, 91%) (Found:  $M^+$ , 471.9268.  $\text{C}_{18}\text{H}_{11}\text{O}_7\text{NCo}_2$  requires  $M$ , 471.9278);  $\nu_{\text{max}}$  (film)/ $\text{cm}^{-1}$  2094, 2054, 2022 ( $\text{C}\equiv\text{O}$ );  $\delta_{\text{H}}$  (250 MHz;  $\text{CDCl}_3$ ) 1.85 (3H, s,  $\text{CCH}_3$ ), 3.38 (1H, d,  $J$  16.7 Hz,  $\text{CCHH}$ ), 3.49 (1H, d,  $J$  16.7 Hz,  $\text{CCHH}$ ), 6.14 (1H, s,  $\text{CCH}$ ), 7.39-7.42 (3H, m,  $\text{ArCH}$ ), 7.64-7.68 (2H, m,  $\text{ArCH}$ );  $\delta_{\text{C}}$  (100 MHz;  $\text{CDCl}_3$ ) 29.7 ( $\text{CCH}_3$ ), 49.3 ( $\text{CCH}_2$ ), 73.1 ( $\text{CCH}$ ), 88.5 ( $\text{CCH}$ ), 99.7 ( $\text{OCC}$ ), 126.3 (2C, s,  $\text{ArCH}$ ), 128.8 ( $\text{ArCH}$ ), 129.6 (2C, s,  $\text{ArCH}$ ), 134.8 ( $\text{ArC}$ ), 156.5 ( $\text{NCCH}_2$ ), peak absent ( $\text{Co}(\text{CO})_3$ );  $m/z$  472 ( $M^+$ , 8%), 443 (13), 415 (35), 387 (40), 359 (25).

**Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-2-methylbut-1-enyne (188)**



Molybdenum cyclopentadienyl tricarbonyl dimer (0.300 g, 0.61 mmol) was dissolved in dry THF (15 mL) in a flame-dried Schlenk flask under an atmosphere of nitrogen. K-Selectride (1.53 mL, 1.53 mmol, 1.0 M in THF) was then added and the mixture stirred for 1.0 h. Dicobalt hexacarbonyl-2-methylbut-1-enyne (0.430 g, 1.22 mmol) in dry THF (20 mL) was then added and the reaction mixture refluxed for 2.0 h. The mixture was cooled, concentrated *in vacuo* and the crude product purified by flash silica chromatography eluting in petroleum ether-diethyl ether (15:1 v/v) to yield the *title complex* as an orange oil (0.355 g, 70%) (Found:  $M^+$ , 427.9001.  $C_{15}H_{11}O_5CoMo$  requires  $M$ , 427.8996);  $\nu_{max}$  (film)/ $cm^{-1}$  2050, 1977, 1920 ( $C\equiv O$ );  $\delta_H$  (250 MHz;  $CDCl_3$ ) 1.91 (3H, s,  $CCH_3$ ), 5.00 (2H, d,  $J$  9.0 Hz,  $CCH_2$ ), 5.36 (5H, s,  $CpH$ ), 5.78 (1H, s,  $CCH$ );  $\delta_c$  (100 MHz;  $CDCl_3$ ) 25.0 ( $CCH_3$ ), 79.1 ( $CHCC$ ), 90.7 ( $CCH$ ), 91.5 ( $CpC$ ), 115.4 ( $CCH_2$ ), 147.8 ( $CHCC$ ), peak absent ( $Co(CO)_3$ ), 225.7, 225.9 ( $MoCp(CO)_2$ );  $m/z$  428 ( $M^+$ , 18%), 400 (45), 372 (100), 344 (35), 316 (24).

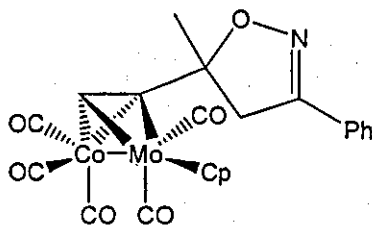
**Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-5-ethynyl-5-methyl-3-phenyl-4,5-dihydroisoxazole (190)**



To benzaldehyde oxime (0.097 g, 0.80 mmol) in  $CHCl_3$  (1 mL) was added *N*-chlorosuccinimide (0.106 g, 0.80 mmol) in  $CHCl_3$  (4 mL) in a 2-neck flame-dried flask under an atmosphere of nitrogen. The reaction mixture was refluxed for 1.0 h at 75°C,

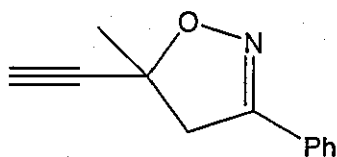
with a colour change generally of pale yellow to a very pale sky blue. After cooling to room temperature cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-2-methylbut-1-enyne (0.113 g, 0.30 mmol) in  $\text{CHCl}_3$  (2 x 1 mL) was added, followed by triethylamine (0.081 g, 0.80 mmol) in  $\text{CHCl}_3$  (3 mL) over 1.0 h, evacuating the evolving HCl gas with nitrogen gas. The reaction mixture was left to stir for 40.0 h. The mixture was then concentrated *in vacuo* and the crude product purified by flash silica chromatography eluting in petroleum ether-diethyl ether (15:1 v/v) to yield the two separable *title complex* diastereoisomers as orange oils ((i) 0.035 g, (ii) 0.035 g, 49%, 1:1 d.r.), (i) First eluting diastereoisomer (Found:  $\text{M}^+$ , 546.9352.  $\text{C}_{22}\text{H}_{16}\text{O}_6\text{NCoMo}$  requires  $\text{M}$ , 546.9364);  $\nu_{\text{max}}$  (film)/ $\text{cm}^{-1}$  2050, 1982, 1939 ( $\text{C}\equiv\text{O}$ );  $\delta_{\text{H}}$  (250 MHz;  $\text{CDCl}_3$ ) 1.71 (3H, s,  $\text{CCH}_3$ ), 3.12 (1H, d,  $J$  16.8 Hz,  $\text{CCHH}$ ), 3.26 (1H, d,  $J$  16.8 Hz,  $\text{CCHH}$ ), 5.39 (5H, s,  $\text{CpH}$ ), 5.81 (1H, s,  $\text{CCH}$ ), 7.39-7.42 (3H, m,  $\text{ArCH}$ ), 7.71-7.74 (2H, m,  $\text{ArCH}$ );  $\delta_{\text{C}}$  (100 MHz;  $\text{CDCl}_3$ ) 31.4 ( $\text{CCH}_3$ ), 48.6 ( $\text{CCH}_2$ ), 81.1 ( $\text{CCH}$ ), 90.7 ( $\text{CpC}$ ), 91.6 ( $\text{CCH}$ ), peak absent ( $\text{OCC}$ ), 126.0 ( $\text{ArC}$ ), 126.7 (2C, s,  $\text{ArCH}$ ), 129.2 (2C, s,  $\text{ArCH}$ ), 130.3 ( $\text{ArCH}$ ), 156.4 ( $\text{ArCN}$ ), 189.8 ( $\text{OCC}$ ), 200.1 ( $\text{Co}(\text{CO})_3$ ), 225.0, 225.8 ( $\text{MoCp}(\text{CO})_2$ );  $m/z$  548 ( $\text{MH}^+$ , 79%), 520 (7), 492 (19). (ii) Second eluting diastereoisomer (Found:  $\text{M}^+-\text{CO}$ , 518.9415.  $\text{C}_{22}\text{H}_{16}\text{O}_6\text{NCoMo}$  requires  $\text{M}-\text{CO}$ , 518.9415);  $\nu_{\text{max}}$  (film)/ $\text{cm}^{-1}$  2092, 2048, 1992 ( $\text{C}\equiv\text{O}$ );  $\delta_{\text{H}}$  (250 MHz;  $\text{CDCl}_3$ ) 1.65 (3H, s,  $\text{CCH}_3$ ), 3.20 (1H, d,  $J$  16.6, Hz,  $\text{CCHH}$ ), 3.37 (1H, d,  $J$  16.6, Hz,  $\text{CCHH}$ ), 5.52 (5H, s,  $\text{CpH}$ ), 5.77 (1H, s,  $\text{CCH}$ ), 7.38-7.41 (3H, m,  $\text{ArCH}$ ), 7.62-7.63 (2H, m,  $\text{ArCH}$ );  $\delta_{\text{C}}$  (100 MHz;  $\text{CDCl}_3$ ) 28.8 ( $\text{CCH}_3$ ), 48.3 ( $\text{CCH}_2$ ), 79.8 ( $\text{CCH}$ ), 89.2 ( $\text{CpC}$ ), 91.1 ( $\text{CCH}$ ), peak absent ( $\text{OCC}$ ), 125.4 (2C, s,  $\text{ArCH}$ ), 127.7 ( $\text{ArCH}$ ), 128.9 (2C, s,  $\text{ArCH}$ ), 129.0 ( $\text{ArC}$ ), 155.0 ( $\text{ArCN}$ ), peak absent ( $\text{Co}(\text{CO})_3$ ), 223.2, 223.7 ( $\text{MoCp}(\text{CO})_2$ );  $m/z$  519 ( $\text{M}^+-\text{CO}$ , 7%), 491 (17), 463 (31), 445 (4).

**Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-5-ethynyl-5-methyl-3-phenyl-4,5-dihydroisoxazole (190)**



Molybdenum cyclopentadienyl tricarbonyl dimer (0.155 g, 0.32 mmol) was dissolved in dry THF (8 mL) in a flame-dried Schlenk flask under an atmosphere of nitrogen. To this, was added K-Selectride (1.27 mL, 1.27 mmol, 1.0 M in THF) and the mixture was stirred for 1.0 h. Dicobalt hexacarbonyl-5-ethynyl-5-methyl-3-phenyl-4,5-dihydroisoxazoline (0.300 g, 0.63 mmol) in THF (2 x 3 mL) was added and the reaction mixture was refluxed for 2.5 h. The mixture was cooled, concentrated *in vacuo* and the crude product purified by flash silica chromatography eluting in petroleum ether-diethyl ether (5:1 v/v) to yield the two separable *title complex* diastereoisomers as orange oils ((i) 0.069 g, (ii) 0.069 g, 40%, 1:1 d.r.). Spectroscopic data were identical with those reported in the previous experiment.

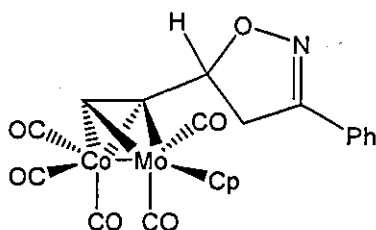
**5-ethynyl-5-methyl-3-phenyl-4, 5-dihydroisoxazole (245)**



Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-5-ethynyl-5-methyl-3-phenyl-4,5-dihydroisoxazole, first-eluting diastereoisomer (0.070 g, 0.13 mmol) in DCM (2 x 5 mL) was added to ceric ammonium nitrate (0.211 g, 0.38 mmol) in a flame-dried Schlenk flask, under an atmosphere of nitrogen at -78°C. Immediately carbon monoxide gas was evolved and the colour changed from a deep orange to a pale yellow. The reaction mixture was stirred for 0.5 h, filtered through a plug of celite and silica, and concentrated *in vacuo* to leave a red liquid. This was triturated with DCM (5 x 2 mL), collecting the DCM fractions, concentrating *in vacuo*, and the residue purified

by flash silica chromatography eluting in petroleum ether-diethyl ether (4:1 v/v) to yield the *title compound* as off white crystals (0.005 g, 21%) (Found:  $M^+$ , 185.0842.  $C_{12}H_{11}NO$  requires  $M$ , 185.0841);  $\nu_{\max}$  (film)/ $cm^{-1}$  3287 ( $C\equiv C-H$ ), 2925 ( $sp^3 C-H$ ), 2117 ( $C\equiv C$ ), 1358 ( $C-O$ );  $\delta_H$  (400 MHz;  $CDCl_3$ ) 1.73 (3H, s,  $CCH_3$ ), 2.67 (1H, s,  $CCH$ ), 3.33 (1H, d,  $J$  16.6 Hz,  $CCHH$ ), 3.64 (1H, d,  $J$  16.6 Hz,  $CCHH$ ), 7.42-7.43 (3H, m,  $ArCH$ ), 7.63-7.65 (2H, m,  $ArCH$ );  $\delta_c$  (100 MHz;  $CDCl_3$ ) 27.5 ( $CCH_3$ ), 48.4 ( $CCH_2$ ), 73.3 ( $CCH$ ), 78.8 ( $CCH$ ), 84.5 ( $OCC$ ), 126.7, 129.1 ( $ArCH$ ), 129.4 ( $ArC$ ), 130.5 ( $ArCH$ ), 156.2 ( $NCCH_2$ );  $m/z$  185 ( $M^+$ , 100%), 170 (21), 155 (25), 565 (24), 142 (20), 119 (60), 91 (36), 77 (59).

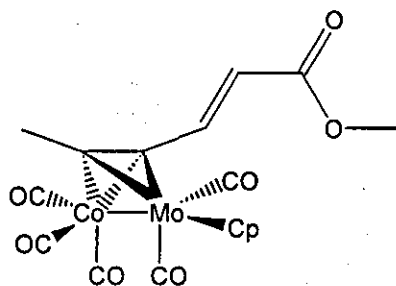
**Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-5-ethynyl-3-phenyl-4,5-dihydroisoxazole (246)**



To benzaldehyde oxime (0.079 g, 0.66 mmol) in  $CHCl_3$  (1 mL) was added *N*-chlorosuccinimide (0.087 g, 0.66 mmol) in  $CHCl_3$  (4 mL) in a 2-neck flame-dried flask under an atmosphere of nitrogen. The reaction mixture was refluxed for 1.0 h at  $75^\circ C$ , with a colour change generally of pale yellow to a very pale sky blue. After cooling to room temperature cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-2-methylbut-1-ene (0.093 g, 0.22 mmol) in  $CHCl_3$  (2 x 1 mL) was added, followed by triethylamine (0.066 g, 0.66 mmol) in  $CHCl_3$  (3 mL) over 1.0 h, evacuating the evolving HCl gas with nitrogen gas. The reaction mixture was left to stir for 40.0 h. The mixture was then concentrated *in vacuo* and the crude product purified by flash silica chromatography eluting in petroleum ether-diethyl ether (15:1 v/v) to yield the two separable *title complex* diastereoisomers as orange oils ((i) 0.025 g, (ii) 0.025 g, 49%, 1:1 d.r.), (i) First eluting diastereoisomer (Found:  $M^+$ , 546.9359.  $C_{22}H_{16}O_6NCoMo$  requires  $M$ , 546.9370);  $\nu_{\max}$  (film)/ $cm^{-1}$  2924 ( $sp^3 C-H$ ), 2048, 1981, 1932 ( $C\equiv O$ );  $\delta_H$  (250 MHz;  $CDCl_3$ ) 2.74 (3H, s,  $CCH_3$ ), 3.04 (1H, dd,  $J$  4.0, 16.0 Hz,  $CHCHH$ ), 3.52 (1H, dd,  $J$  12.0, 16.0 Hz,  $CHCHH$ ), 5.36 (5H, s,  $CpH$ ), 5.94 (1H, dd,  $J$

5.3, 15.1 Hz, CCH), 7.41-7.42 (3H, m, ArCH), 7.67-7.68 (2H, m, ArCH);  $\delta_c$  (100 MHz; CDCl<sub>3</sub>) 20.6 (CCH<sub>3</sub>), 41.3 (CHCH<sub>2</sub>), 85.7 (CCH), 90.8 (CpC), 83.6, 98.7 (CH<sub>3</sub>C, CCC), 126.9 (2C, s, ArCH), 129.2 (2C, s, ArCH), 130.0 (ArC), 130.4 (ArCH), 156.4 (ArCN), peak absent (Co(CO)<sub>3</sub>), 224.8, 225.5 (MoCp(CO)<sub>2</sub>);  $m/z$  547 (M<sup>+</sup>, 10%), 519 (12), 490 (36), 463 (46), 435 (8), 406 (100). (ii) Second eluting diastereoisomer (Found: M<sup>+</sup>-2CO, 490.9479. C<sub>22</sub>H<sub>16</sub>O<sub>6</sub>NCoMo requires M-2CO, 490.9470);  $\nu_{\max}$  (film)/cm<sup>-1</sup> 2925 (sp<sup>3</sup> C-H), 2047, 1979, 1933 (C≡O);  $\delta_H$  (250 MHz; CDCl<sub>3</sub>) 2.71 (3H, s, CCH<sub>3</sub>), 3.12 (1H, dd,  $J$  6.3, 16.4 Hz, CHCHH), 3.45 (1H, dd,  $J$  10.4, 16.4 Hz, CHCHH), 5.46 (5H, s, CpH), 5.70 (1H, d,  $J$  16.6 Hz, CCH), 7.40-7.43 (3H, m, ArCH), 7.66-7.68 (2H, m, ArCH);  $\delta_c$  (100 MHz; CDCl<sub>3</sub>) 20.4 (CCH<sub>3</sub>), 42.4 (CHCH<sub>2</sub>), 85.1 (CCH), 90.7 (CpC), 87.4 (CCH<sub>3</sub>), 99.6 (CCC), 127.0 (2C, s, ArCH), 129.2 (2C, s, ArCH), 129.9 (ArC), 130.5 (ArCH), 156.6 (ArCN), peak absent (Co(CO)<sub>3</sub>), 224.2, 226.4 (MoCp(CO)<sub>2</sub>);  $m/z$  519 (M<sup>+</sup>-CO, 5%), 491 (17), 463 (17), 435 (7), 407 (50).

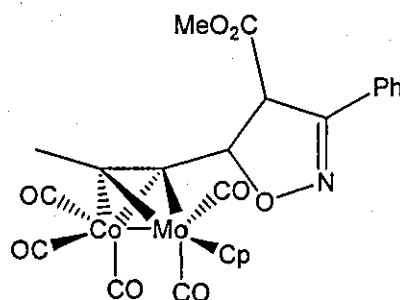
**Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-methyl-(*E*)-hex-2-en-4-ynoate (187)**



Molybdenum cyclopentadienyl tricarbonyl dimer (0.107 g, 0.22 mmol) was dissolved in dry THF (15 mL) in a flame-dried Schlenk flask under an atmosphere of nitrogen. To this, was added K-Selectride (0.54 mL, 0.54 mmol, 1.0 M in THF) and the reaction mixture was stirred for 1.0 h. Dicobalt hexacarbonyl-methyl-(*E*)-hex-2-en-4-ynoate (0.180 g, 0.44 mmol) in THF (5 mL) was added and the mixture refluxed for 2.0 h. The crude product was cooled, concentrated *in vacuo* and purified by flash silica chromatography eluting in petroleum ether-diethyl ether (15:1 v/v) to yield the *title complex* as a red/orange oil (0.164 g, 78%) (Found: M<sup>+</sup>, 485.9050. C<sub>17</sub>H<sub>13</sub>O<sub>7</sub>CoMo requires M, 485.9052);  $\nu_{\max}$  (film)/cm<sup>-1</sup> 2952 (sp<sup>3</sup> C-H), 2051, 1981, 1940 (C≡O), 1713 (C=O);  $\delta_H$  (250 MHz; CDCl<sub>3</sub>) 2.69 (3H, s, CCH<sub>3</sub>), 3.75 (3H, s, CH<sub>3</sub>CO<sub>2</sub>), 5.35 (5H, s,

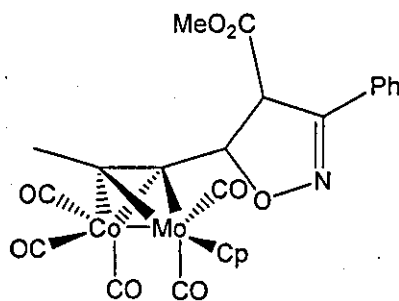
CpH), 5.81 (1H, d,  $J$  15.3 Hz, CCHCH), 7.86 (1H, d,  $J$  15.3 Hz, CHCO<sub>2</sub>CH<sub>3</sub>);  $\delta_c$  (100 MHz; CDCl<sub>3</sub>) 21.2 (CCH<sub>3</sub>), 51.8 (CH<sub>3</sub>CO<sub>2</sub>), 82.4 (CCCH), 91.5 (CpC), 101.8 (CCH<sub>3</sub>), 119.5 (CCHCH), 151.0 (CHCO<sub>2</sub>CH<sub>3</sub>), 167.5 (CH<sub>3</sub>CO<sub>2</sub>), peak absent (Co(CO)<sub>3</sub>), 223.6, 225.3 (MoCp(CO)<sub>2</sub>);  $m/z$  486 (M<sup>+</sup>, 2%), 456 (7), 428 (19), 400 (27).

**Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-methyl-3-phenyl-5-propynyl-4,5-dihydroisoxazole-4-carboxylate (189)**



To benzaldehyde oxime (0.075 g, 0.71 mmol) in CHCl<sub>3</sub> (1 mL) was added *N*-chlorosuccinimide (0.083 g, 0.71 mmol) in CHCl<sub>3</sub> (3 mL) in a 2-neck flame-dried flask under an atmosphere of nitrogen. The reaction mixture was refluxed for 1.0 h at 75°C, with a colour change generally of pale yellow to a very pale sky blue. After cooling to room temperature cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-methyl-(*E*)-hex-2-en-4-ynoate (0.100 g, 0.28 mmol) in CHCl<sub>3</sub> (2 x 1 mL) was added, followed by triethylamine (0.063 g, 0.71 mmol) in CHCl<sub>3</sub> (3 mL) over 1.0 h, evacuating the evolving HCl gas with nitrogen gas. The reaction mixture was left to stir for 24.0 h. The mixture was then concentrated *in vacuo* and the crude product purified by flash silica chromatography eluting in petroleum ether-diethyl ether (5:1 v/v) to yield the two inseparable *title complex* diastereoisomers as a deep orange oil (0.009 g, 7%, 1:1 d.r.). Spectroscopic data were identical with those reported in the following experiment.

**Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-methyl-3-phenyl-5-propynyl-4,5-dihydroisoxazoline-4-carboxylate (189)**

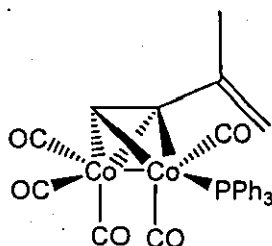


Molybdenum cyclopentadienyl tricarbonyl dimer (0.227 g, 0.46 mmol) was dissolved in dry THF (10 mL) in a flame-dried Schlenk flask under an atmosphere of nitrogen. To this, was added K-Selectride (1.10 mL, 1.10 mmol, 1.0 M in THF) and the mixture was stirred for 1.0 h. Dicobalt hexacarbonyl-methyl-3-phenyl-5-propynyl-4,5-dihydroisoxazole-4-carboxylate (0.448 g, 0.93 mmol) in THF (2 x 5 mL) was added and the reaction mixture, then refluxed for 2.5 h. The crude product was cooled, the mixture concentrated *in vacuo* and the crude product purified by flash silica chromatography eluting in petroleum ether-diethyl ether (5:1 v/v) to yield the two separable *title complex* diastereoisomers as deep orange oils ((i) 0.104 g, (ii) 0.104 g, 40%, 1:1 d.r.), (i) First eluting diastereoisomer (Found:  $M^+-2CO$ , 548.9529.  $C_{24}H_{18}O_8NCoMo$  requires  $M-2CO$ , 548.9520);  $\nu_{max}$  (film)/ $cm^{-1}$  2924 ( $sp^3$  C-H), 2051, 1984, 1936 ( $C\equiv O$ ), 1741 ( $C=O$ );  $\delta_H$  (400 MHz;  $CDCl_3$ ) 2.76 (3H, s,  $CCH_3$ ), 3.73 (3H, s,  $CH_3CO_2$ ), 4.14 (1H, d,  $J$  4.8 Hz,  $CHCO_2Me$ ), 5.35 (5H, s,  $CpH$ ), 6.06 (1H, d,  $J$  4.8 Hz,  $OCH$ ), 7.37-7.42 (3H, m,  $ArCH$ ), 7.69-7.72 (2H, m,  $ArCH$ );  $\delta_c$  (100 MHz;  $CDCl_3$ ) 20.2 ( $CCH_3$ ), 53.1 ( $CO_2CH_3$ ), 59.6 ( $CHCO_2CH_3$ ), 84.8 ( $OCH$ ), 90.3 ( $CpC$ ), 90.5 ( $CCH_3$ ), 99.2 ( $CHCC$ ), 126.7 (2C, s,  $ArCH$ ), 128.8 ( $ArC$ ), 129.0 (2C, s,  $ArCH$ ), 130.4 ( $ArCH$ ), 153.6 ( $NCCH_2$ ), 169.3 ( $CO_2CH_3$ ), 213.2 ( $Co(CO)_3$ ), 224.6, 224.8 ( $MoCp(CO)_2$ );  $m/z$  549 ( $M^+-2CO$ , 13%), 521 (69), 465 (11), 437 (17). (ii) Second eluting diastereoisomer (Found:  $M^+-3CO$ , 520.9577.  $C_{24}H_{18}O_8NCoMo$  requires  $M-3CO$ , 520.9571);  $\nu_{max}$  (film)/ $cm^{-1}$  2948 ( $sp^3$  C-H), 2054, 1992, 1941 ( $C\equiv O$ ), 1734 ( $C=O$ );  $\delta_H$  (400 MHz;  $CDCl_3$ ) 2.69 (3H, s,  $CCH_3$ ), 3.74 (3H, s,  $CH_3CO_2$ ), 4.24 (1H, d,  $J$  5.4 Hz,  $CHCO_2CH_3$ ), 5.45 (5H, s,  $CpH$ ), 5.88 (1H, d,  $J$  5.4 Hz,  $OCH$ ), 7.37-7.42 (3H, m,  $ArCH$ ), 7.52-7.54 (2H, m,  $ArCH$ );  $\delta_c$  (100 MHz;  $CDCl_3$ ) 20.0 ( $CCH_3$ ), 50.1 ( $CO_2CH_3$ ), 60.7 ( $CHCO_2CH_3$ ), 84.8 ( $OCH$ ), 90.0 ( $CHCC$ ), 90.4 ( $CpC$ ), 99.0 ( $CCH_3$ ),



126.7 (2C, s, ArCH), 128.6 (ArC), 128.9 (2C, s, ArCH), 130.3 (ArCH), 153.7 (NCCH<sub>2</sub>), 169.5 (CO<sub>2</sub>CH<sub>3</sub>), 203.2 (Co(CO)<sub>3</sub>), 223.6, 225.5 (MoCp(CO)<sub>2</sub>); *m/z* 605 (M<sup>+</sup>, 7%), 577 (7), 549 (12), 521 (56), 465 (12).

**Dicobalt pentacarbonyl triphenylphosphine-2-methylbut-1-enyne (249)**

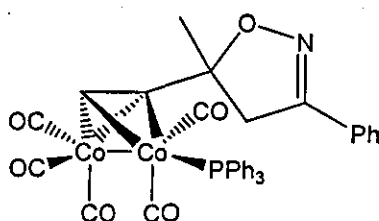


Dicobalt hexacarbonyl-2-methylbut-1-enyne (0.408 g, 1.16 mmol) in dry THF/diethyl ether (2:1 v/v, 20 mL) was added to a flame-dried flask under an atmosphere of nitrogen and heated to 50°C. To this was added triphenylphosphine (0.243 g, 0.93 mmol) in dry THF/diethyl ether (2:1 v/v, 10 mL) over 1.0 h and stirred until no triphenylphosphine was present on TLC, at which time the mixture was cooled, concentrated *in vacuo* and the crude product purified by flash silica chromatography eluting in petroleum ether-diethyl ether (15:1 v/v) to yield the *title complex* as a deep red oil (0.295 g, 55%) (Found: M<sup>+</sup>, 585.9775. C<sub>28</sub>H<sub>21</sub>O<sub>5</sub>Co<sub>2</sub>P requires M, 585.9791);  $\nu_{\max}$  (film)/cm<sup>-1</sup> 2059, 2002, 1961 (C≡O);  $\delta_{\text{H}}$  (250 MHz; CDCl<sub>3</sub>) 1.77 (3H, s, CCH<sub>3</sub>), 4.91 (1H, s, CCHH), 4.99 (1H, s, CCHH), 5.29 (1H, t, *J* 7.6 Hz, CCH), 7.36-7.44 (15H, m, ArCH);  $\delta_{\text{C}}$  (100 MHz; CDCl<sub>3</sub>) 22.9 (CCH<sub>3</sub>), 70.5 (CCH), 87.1 (CHCC), 115.8 (CCH<sub>2</sub>), 127.4 (2C, d, <sup>3</sup>*J*<sub>P-C</sub> 22.0 Hz, ArCH), 129.1 (1C, d, <sup>4</sup>*J*<sub>P-C</sub> 2.0 Hz, ArCH), 132.0 (2C, d, <sup>2</sup>*J*<sub>P-C</sub> 22.0 Hz, ArCH), 133.5 (1C, d, <sup>1</sup>*J*<sub>P-C</sub> 42.0 Hz, ArC), 140.7 (CHCC), 200.7 (Co(CO)<sub>3</sub>); *m/z* 586 (M<sup>+</sup>, 5%), 530 (10), 474 (100), 446 (100).

The diphosphinated species **250** was also isolated as a dark red oil (0.178 g, 23%) (Found: M<sup>+</sup>, 820.0770. C<sub>45</sub>H<sub>36</sub>O<sub>4</sub>Co<sub>2</sub>P<sub>2</sub> requires M, 820.0753);  $\nu_{\max}$  (film)/cm<sup>-1</sup> 2014, 1955 (C≡O);  $\delta_{\text{H}}$  (250 MHz; CDCl<sub>3</sub>) 1.29 (3H, s, CCH<sub>3</sub>), 4.47 (1H, t, *J* 7.6 Hz, CCH), 4.54 (2H, d, *J* 17.6 Hz, CCH<sub>2</sub>), 7.36 (30H, m, ArCH);  $\delta_{\text{C}}$  (100 MHz; CDCl<sub>3</sub>) 24.5 (CCH<sub>3</sub>), 71.4 (CCH), 83.9 (CHCC), 117.0 (CCH<sub>2</sub>), 128.4 (2C, d, <sup>3</sup>*J*<sub>P-C</sub> 9.0 Hz, ArCH), 129.9 (1C, s, ArCH), 133.6 (2C, d, <sup>2</sup>*J*<sub>P-C</sub> 11.0 Hz, ArCH), 136.0 (1C, d, <sup>1</sup>*J*<sub>P-C</sub> 38.0 Hz,

ArC), 142.9 (CHCC), 207.3, 207.6 (Co(CO)<sub>3</sub>); *m/z* 820 (M<sup>+</sup>, 2%), 792 (89), 764 (5), 736 (1), 708 (20).

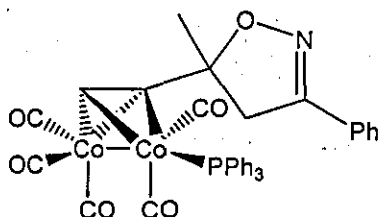
**Dicobalt pentacarbonyl triphenylphosphine-5-ethynyl-5-methyl-3-phenyl-4,5-dihydroisoxazole (253)**



To benzaldehyde oxime (0.113 g, 0.90 mmol) in CHCl<sub>3</sub> (1 mL) was added *N*-chlorosuccinimide (0.124 g, 0.90 mmol) in CHCl<sub>3</sub> (3 mL) in a 2-neck flame-dried flask under an atmosphere of nitrogen. The reaction mixture was then refluxed for 1.0 h at 75°C, with a colour change generally of pale yellow to a very pale sky blue. After cooling to room temperature dicobalt pentacarbonyl triphenylphosphine-2-methylbut-1-enyne (0.182 g, 0.30 mmol) in CHCl<sub>3</sub> (2 x 1 mL) was added, followed by triethylamine (0.094 g, 0.90 mmol) in CHCl<sub>3</sub> (2 mL) over 1.0 h, evacuating the evolving HCl gas with nitrogen gas. The reaction mixture was left to stir for 24.0 h. The mixture was then concentrated *in vacuo* and the crude product purified by flash silica chromatography eluting in petroleum ether-diethyl ether (10:1 v/v) to yield the two inseparable *title complex* diastereoisomers as a deep red oil (0.033 g, 15%, 1:1 d.r.) (Found: M<sup>+</sup>, 705.0152. C<sub>35</sub>H<sub>26</sub>O<sub>6</sub>NPCo<sub>2</sub> requires M, 705.0162); *v*<sub>max</sub> (film)/cm<sup>-1</sup> 2063, 2000, 1957 (C≡O); δ<sub>H</sub> (400 MHz; CDCl<sub>3</sub>) 1.41 (3H, s, CCH<sub>3</sub>), 1.60 (3H, s, CCH<sub>3</sub>), 2.84 (1H, d, *J* 16.4 Hz, CCHH), 2.90 (1H, d, *J* 16.4 Hz, CCHH), 3.06 (1H, d, *J* 16.6 Hz, CCHH), 3.23 (1H, d, *J* 16.6 Hz, CCHH), 5.19-5.23 (2H, m, CCH), 7.28-7.57 (40H, m, ArCH); δ<sub>c</sub> (100 MHz; CDCl<sub>3</sub>) 29.6, 29.8 (CCH<sub>3</sub>), 49.0, 49.2 (CCH<sub>2</sub>), 73.7, 74.3 (CCH), 89.0, 89.1 (CCH), 94.5, 95.5 (OCC), 126.9 (1C, d, <sup>4</sup>*J*<sub>P-C</sub> 2.0 Hz, ArCH), 128.88 (2C, d, <sup>3</sup>*J*<sub>P-C</sub> 10.0 Hz, ArCH), 128.93 (2C, s, ArCH), 128.95 (2C, d, <sup>3</sup>*J*<sub>P-C</sub> 10.0 Hz, ArCH), 128.99 (2C, s, ArCH), 130.1 (2 x ArCH), 130.48, 130.50 (ArC), 130.6 (1C, d, <sup>4</sup>*J*<sub>P-C</sub> 2.0 Hz, ArCH),

133.5 (2C, d,  $^2J_{P-C}$  11.0 Hz, ArCH), 133.6 (2C, d,  $^2J_{P-C}$  11.0 Hz, ArCH), 135.3 (1C, d,  $^1J_{P-C}$  40.0 Hz, ArC), 135.4 (1C, d,  $^1J_{P-C}$  40.0 Hz, ArC), 156.2, 156.3 (NCCH<sub>2</sub>), 201.3 (Co(CO)<sub>3</sub>;  $m/z$  705 (M<sup>+</sup>, 2%), 621 (23), 593 (52), 565 (24).

**Dicobalt pentacarbonyl triphenylphosphine-5-ethynyl-5-methyl-3-phenyl-4,5-dihydroisoxazole (253)**

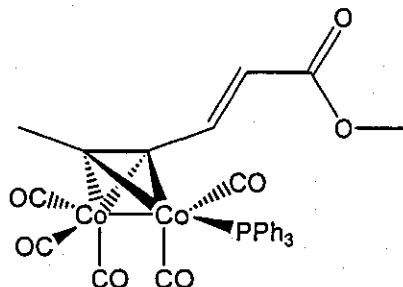


Dicobalt hexacarbonyl-5-ethynyl-5-methyl-3-phenyl-4,5-dihydroisoxazole (0.241 g, 0.51 mmol) in dry THF/diethyl ether (2:1 v/v, 20 mL) was added to a flame-dried flask under an atmosphere of nitrogen and heated to 50°C. To this was added triphenylphosphine (0.107 g, 0.41 mmol) in dry THF/diethyl ether (2:1 v/v, 10 mL) over 1.0 h and the mixture stirred until no triphenylphosphine was present by TLC, at which time the mixture was cooled, concentrated *in vacuo* and the crude product purified by flash silica chromatography eluting in petroleum ether-diethyl ether (10:1 v/v) to yield the two inseparable *title complex* diastereoisomers as a deep red oil (0.081 g, 28%, 1:1 d.r.). Spectroscopic data were identical with those reported in the previous experiment.

The diphosphinated species **254** was also isolated as a dark red oil (0.059 g, 10%) (Found: M<sup>+</sup>-CO, 911.1162. C<sub>52</sub>H<sub>41</sub>O<sub>5</sub>Co<sub>2</sub>NP<sub>2</sub> requires M-CO, 911.1175);  $\nu_{\max}$  (film)/cm<sup>-1</sup> 2016, 1992, 1958 (C≡O);  $\delta_H$  (250 MHz; CDCl<sub>3</sub>) 1.43 (3H, s, CCH<sub>3</sub>), 2.70 (1H, d,  $J$  16.6 Hz, CCHH), 3.00 (1H, d,  $J$  16.6 Hz, CCHH), 4.44 (1H, t,  $J$  5.2 Hz, CCH), 7.33-7.46 (35H, m, ArCH);  $\delta_c$  (100 MHz; CDCl<sub>3</sub>) 29.4 (CCH<sub>3</sub>), 49.1 (CCH<sub>2</sub>), 73.3 (CCH), 89.3 (CCH), 92.1 (OCCH<sub>2</sub>), 126.4, 128.1, 128.3, 128.5, 129.5 (ArCH),

130.5 (ArC), 133.3 (ArCH), 136.1 (1C, d,  $^1J_{P-C}$  36.0 Hz, ArC), 155.5 (CHCC), 206.9 (Co(CO)<sub>3</sub>);  $m/z$  911 (M<sup>+</sup>-CO, 5%), 882 (4), 855 (2), 827 (37).

**Dicobalt pentacarbonyl triphenylphosphine-methyl-(E)-hex-2-en-4-ynoate (251)**

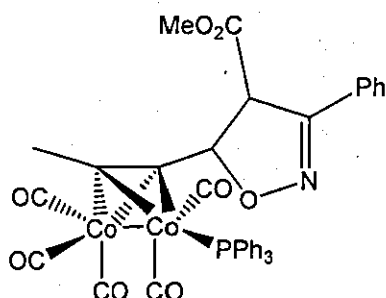


Dicobalt hexacarbonyl-methyl-(E)-hex-2-en-4-ynoate (0.206 g, 0.50 mmol) in THF/diethyl ether (2:1 v/v, 20 mL) was added to a flame-dried flask under an atmosphere of nitrogen and heated to 50°C. To this was added triphenylphosphine (0.105 g, 0.40 mmol) in THF/diethyl ether (2:1 v/v, 10 mL) over 1.0 h and the mixture stirred until no triphenylphosphine was present by TLC. The crude product was then cooled, concentrated *in vacuo* and purified by flash silica chromatography eluting in petroleum ether-diethyl ether (15:1 v/v) to yield the *title complex* as a deep red oil (0.270 g, 58%) (Found: M<sup>+</sup>, 643.9857. C<sub>30</sub>H<sub>23</sub>O<sub>7</sub>PCo<sub>2</sub> requires M, 643.9846);  $\nu_{\max}$  (film)/cm<sup>-1</sup> 2061, 2006, 1962 (C≡O), 1717 (C=O);  $\delta_H$  (250 MHz; CDCl<sub>3</sub>) 2.12 (3H, s, CCH<sub>3</sub>), 3.70 (3H, s, CH<sub>3</sub>CO<sub>2</sub>), 5.76 (1H, d,  $J$  15.3 Hz, CCHCH), 7.30 (1H, d,  $J$  15.3 Hz, CHCO<sub>2</sub>CH<sub>3</sub>), 7.39-7.49 (15H, m, ArCH);  $\delta_c$  (100 MHz; CDCl<sub>3</sub>) 20.3 (CCH<sub>3</sub>), 51.7 (CH<sub>3</sub>CO<sub>2</sub>), 81.3 (CCCH<sub>3</sub>), 91.9 (CCCH), 120.6 (CCHCH), 129.0 (2C, d,  $^3J_{P-C}$  10.0 Hz, ArCH), 130.8 (ArCH), 133.5 (2C, d,  $^2J_{P-C}$  11.0 Hz, ArCH), 134.6 (1C, d,  $^1J_{P-C}$  42.0 Hz, ArC), 147.0 (CHCO<sub>2</sub>CH<sub>3</sub>), 167.4 (CH<sub>3</sub>CO<sub>2</sub>), 201.3 (Co(CO)<sub>3</sub>), 204.8, 205.8 (Co(CO)<sub>2</sub>);  $m/z$  644 (M<sup>+</sup>, 2%), 616 (1), 588 (15), 560 (24).

The diphosphinated species **252** was also isolated as a deep red oil (0.200 g, 26%) (Found: M<sup>+</sup>-CO, 850.0849. C<sub>47</sub>H<sub>38</sub>O<sub>6</sub>P<sub>2</sub>Co<sub>2</sub> requires M-CO, 850.0859);  $\nu_{\max}$  (film)/cm<sup>-1</sup> 2015, 1971, 1956 (C≡O), 1700 (C=O);  $\delta_H$  (250 MHz; CDCl<sub>3</sub>) 1.48 (3H, s, CCH<sub>3</sub>), 3.56 (3H, s, CH<sub>3</sub>CO<sub>2</sub>), 4.94 (1H, d,  $J$  15.3 Hz, CCHCH), 7.07 (1H, d,  $J$  15.3 Hz, CHCO<sub>2</sub>CH<sub>3</sub>), 7.28-7.35 (18H, m, ArCH), 7.37-7.45 (12H, m, ArCH);  $\delta_c$  (100 MHz; CDCl<sub>3</sub>) 18.9 (CCH<sub>3</sub>), 51.3 (CH<sub>3</sub>CO<sub>2</sub>), 74.4 (CCCH<sub>3</sub>), 84.3 (CCCH), 118.5 (CCHCH),

128.6 (ArCH), 130.1 (ArCH), 133.6 (2C, d,  $^2J_{P-C}$  10.0 Hz, ArCH), 135.3 (1C, d,  $^1J_{P-C}$  39.0 Hz, ArC), 147.6 (CHCO<sub>2</sub>CH<sub>3</sub>), 167.3 (CH<sub>3</sub>CO<sub>2</sub>), 206.8, 207.5 (Co(CO)<sub>2</sub>); *m/z* 850 (M<sup>+</sup>-CO, 4%), 823 (10), 767 (56), 505 (100).

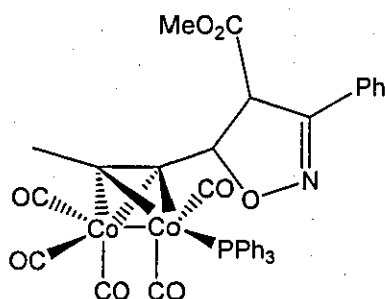
**Dicobalt pentacarbonyl triphenylphosphine-methyl-3-phenyl-5-propynyl-4,5-dihydroisoxazoline-4-carboxylate (255)**



To benzaldehyde oxime (0.053 g, 0.40 mmol) in CHCl<sub>3</sub> (1 mL) was added *N*-chlorosuccinimide (0.060 g, 0.40 mmol) in CHCl<sub>3</sub> (2 mL) in a 2-neck flame-dried flask under an atmosphere of nitrogen. The reaction mixture was refluxed for 1.0 h at 75°C, with a colour change generally of pale yellow to a very pale sky blue. After cooling to room temperature dicobalt pentacarbonyl triphenylphosphine-methyl-(*E*)-hex-2-en-4-ynoate (0.098 g, 0.20 mmol) in CHCl<sub>3</sub> (2 x 1 mL) was added, followed by triethylamine (0.045 g, 0.40 mmol) in CHCl<sub>3</sub> (2 mL) over 0.5 h, evacuating the evolving HCl gas with nitrogen gas. The reaction mixture was then left to stir for 24.0 h. The mixture was concentrated *in vacuo* and the crude product purified by flash silica chromatography eluting in petroleum ether-diethyl ether (5:1 v/v) to yield the inseparable *title complex* diastereoisomers as a dark red oil (0.021 g, 20%, 2:1 d.r.) (Found: M<sup>+</sup>-2CO, 707.0323. C<sub>37</sub>H<sub>28</sub>O<sub>8</sub>NPCo<sub>2</sub> requires M-2CO, 707.0319);  $\nu_{\max}$  (film)/cm<sup>-1</sup> 2060, 2008 (C≡O), 1741 (C=O); Assigned from combined spectrum (i) Major diastereoisomer  $\delta_H$  (250 MHz; CDCl<sub>3</sub>) 2.05 (3H, s, CCH<sub>3</sub>), 3.59 (3H, s, CH<sub>3</sub>CO<sub>2</sub>), 4.01 (1H, d, *J* 6.3 Hz, CCH), 5.16 (1H, dd, *J* 2.3, 4.4 Hz, OCH), 7.32-7.75 (20H, m, ArCH). (ii) Minor diastereoisomer  $\delta_H$  (250 MHz; CDCl<sub>3</sub>) 2.18 (3H, s, CCH<sub>3</sub>), 3.65 (3H, s, CH<sub>3</sub>CO<sub>2</sub>), 4.46 (1H, d, *J* 4.6 Hz, CCH), 5.24 (1H, dd, *J* 0.9, 6.2 Hz, OCH), 7.32-7.75 (20H, m, ArCH); (i, ii)  $\delta_c$  (100 MHz; CDCl<sub>3</sub>) 19.5, 20.3 (CCH<sub>3</sub>), 53.1, 53.2 (CO<sub>2</sub>CH<sub>3</sub>), 60.3, 61.4 (CCHO), 86.1, 86.6 (CHCO<sub>2</sub>CH<sub>3</sub>), 88.3, 89.6, 90.1, 91.5 (CCH<sub>3</sub>, CHCC), 127.1, 127.4 (ArCH), 128.9 (ArC), 129.1 (1C, d,  $^4J_{P-C}$  10.0 Hz, ArCH),

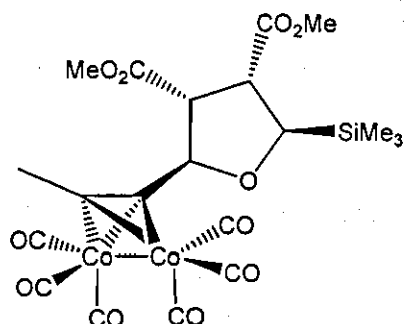
129.05, 129.08 (ArCH), 129.2 (1C, d,  $^4J_{P-C}$  10.0 Hz, ArCH), 130.4, 130.5 (ArCH), 130.8 (2C, d,  $^3J_{P-C}$  10.0 Hz, ArCH), 130.9 (2C, d,  $^3J_{P-C}$  10.0 Hz, ArCH), 133.4 (2C, d,  $^2J_{P-C}$  21.0 Hz, ArCH), 133.5 (2C, d,  $^2J_{P-C}$  21.0 Hz, ArCH), 134.7 (1C, d,  $^1J_{P-C}$  41.0 Hz, ArCH), 134.8 (1C, d,  $^1J_{P-C}$  41.0 Hz, ArCH), 153.4, 153.5 (CO<sub>2</sub>CH<sub>3</sub>), 169.6, 169.8 (NCCH<sub>2</sub>), 201.3 (Co(CO)<sub>3</sub>);  $m/z$  765 (M<sup>+</sup>, 12%), 737 (3), 707 (15), 679 (71), 651 (100), 623 (75).

**Dicobalt pentacarbonyl triphenylphosphine-methyl-3-phenyl-5-propynyl-4,5-dihydroisoxazole-4-carboxylate (255)**



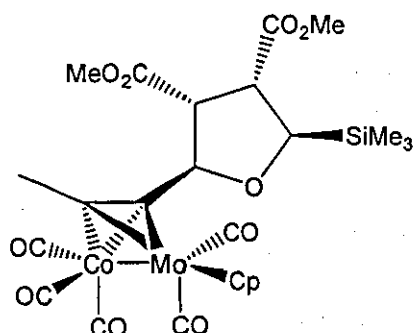
Dicobalt hexacarbonyl-methyl-3-phenyl-5-propynyl-4,5-dihydroisoxazole-4-carboxylate (0.098 g, 0.19 mmol) in dry THF/diethyl ether (2:1 v/v, 10 mL) was added to a flame-dried flask under an atmosphere of nitrogen and heated to 50°C. To this was added triphenylphosphine (0.039 g, 0.15 mmol) in dry THF/diethyl ether (2:1 v/v, 5 mL) over 1.0 h and the mixture stirred until no triphenylphosphine was present by TLC, at which time the mixture was cooled, concentrated *in vacuo* and the crude product purified by flash silica chromatography eluting in petroleum ether-diethyl ether (3:1 v/v) to yield the two inseparable *title complex* diastereoisomers as a dark red oil (0.067 g, 59%, 1:1 d.r.). Spectroscopic data were identical with those reported in the previous experiment.

**Dicobalt hexacarbonyl-1-(tetrahydrofuran-2,3-dicarboxylic acid dimethyl ester-4-trimethylsilyl)propyne (257)<sup>104</sup>**



To a flame-dried 2-neck RBF under an atmosphere of nitrogen was added dimethyl maleate (0.22 mL, 2.22 mmol),  $\text{Rh}_2(\text{OAc})_4$  (0.014 g, 0.03 mmol) and dicobalt hexacarbonyl-butyne (0.400 g, 1.13 mmol) in DCM (5 mL). (Trimethylsilyl)diazomethane (1.20 mL, 2.22 mmol) in DCM (5 mL) was added to the reaction mixture over 6.0 h whilst stirring. After stirring for a further 0.5 h the crude mixture was filtered through a plug of celite and silica. The solvent was removed *in vacuo* to leave a red oil, which was purified by flash silica chromatography eluting in petroleum ether-diethyl ether (6:1 v/v) to yield a single *title complex* diastereoisomer as a red oil (0.363 g, 44%) (Found:  $\text{M}^+ - 2\text{CO}$ , 527.9688.  $\text{C}_{20}\text{H}_{22}\text{O}_{11}\text{Co}_2\text{Si}$  requires  $\text{M} - 2\text{CO}$ , 527.9697);  $\nu_{\text{max}}$  (film)/ $\text{cm}^{-1}$  2016, 2005 ( $\text{C}\equiv\text{O}$ ), 1744 ( $\text{C}=\text{O}$ );  $\delta_{\text{H}}$  (250 MHz;  $\text{CDCl}_3$ ) 0.07 (9H, s,  $\text{Si}(\text{CH}_3)_3$ ), 2.63 (3H, s,  $\text{CCH}_3$ ), 2.89 (1H, dd,  $J$  9.0, 10.9 Hz,  $\text{CHCO}_2\text{CH}_3$ ), 3.37 (1H, dd,  $J$  9.5, 10.6 Hz,  $\text{CHCO}_2\text{CH}_3$ ), 3.68, 3.70 (3H, s,  $\text{CO}_2\text{CH}_3$ ), 3.85 (1H, d,  $J$  8.6 Hz,  $\text{OCHSi}$ ), 5.15 (1H, d,  $J$  9.0 Hz,  $\text{OCHC}$ );  $\delta_{\text{C}}$  (100 MHz;  $\text{CDCl}_3$ ) -3.9 (3C, s,  $\text{Si}(\text{CH}_3)_3$ ), 20.9 ( $\text{CCH}_3$ ), 50.2 ( $\text{CHCO}_2\text{CH}_3$ ), 52.4 (2C, s,  $\text{C}(\text{CO}_2\text{CH}_3)_2$ ), 56.4 ( $\text{CHCO}_2\text{CH}_3$ ), 75.2 ( $\text{CHSi}$ ), 82.3 ( $\text{CHCC}$ ), 94.1 ( $\text{CCCH}_3$ ), 94.6 ( $\text{CH}_3\text{CC}$ ), 171.1, 172.9 ( $\text{CO}_2\text{CH}_3$ ), 199.9 ( $\text{Co}(\text{CO})_3$ );  $m/z$  556 ( $\text{M}^+ - \text{CO}$ , 7%), 528 (88), 500 (100), 472 (73), 444 (25).

**Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-1-(tetrahydrofuran-2,3-dicarboxylic acid dimethyl ester-4-trimethylsilyl)propyne (191)**

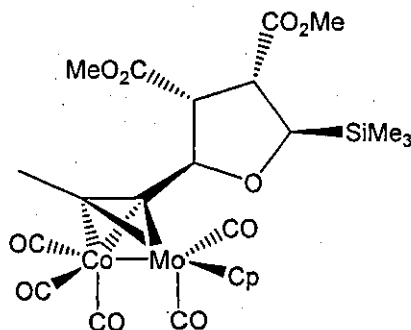


To a flame-dried 2-neck RBF under an atmosphere of nitrogen was added dimethyl maleate (0.12 mL, 1.16 mmol),  $\text{Rh}_2(\text{OAc})_4$  (0.007 g, 0.02 mmol) and cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-butynal (0.250 g, 0.58 mmol) in DCM (5 mL). (Trimethylsilyl)diazomethane (0.60 mL, 1.16 mmol) in DCM (3 mL) was added to the reaction mixture over 6.0 h, whilst stirring at reflux. After stirring for a further 0.5 h the crude mixture was filtered through a plug of celite and silica. The solvent was removed *in vacuo* to leave a red oil, which was purified by flash silica chromatography eluting in petroleum ether-diethyl ether (10:1 v/v) to yield the two separable *title complex* diastereoisomers as red oils ((i) 0.014 g, (ii) 0.014 g, 10%, 1:1 d.r.), (i) First eluting diastereoisomer (Found:  $\text{M}^+-3\text{CO}$ , 603.9847.  $\text{C}_{24}\text{H}_{27}\text{O}_{10}\text{CoMoSi}$  requires  $\text{M}-3\text{CO}$ , 603.9861);  $\nu_{\text{max}}$  (film)/ $\text{cm}^{-1}$  2045, 1977, 1932 ( $\text{C}\equiv\text{O}$ ), 1745 ( $\text{C}=\text{O}$ );  $\delta_{\text{H}}$  (250 MHz;  $\text{CDCl}_3$ ) 0.07 (9H, s,  $\text{Si}(\text{CH}_3)_3$ ), 2.63 (3H, s,  $\text{CCH}_3$ ), 2.91 (1H, dd,  $J$  8.7, 11.2 Hz,  $\text{CHCO}_2\text{CH}_3$ ), 3.28 (1H, t,  $J$  10.8 Hz,  $\text{CHCO}_2\text{CH}_3$ ), 3.66, 3.68 (3H, s,  $\text{CO}_2\text{CH}_3$ ), 3.78 (1H, d,  $J$  10.4 Hz,  $\text{OCHSi}$ ), 4.91 (1H, d,  $J$  8.6 Hz,  $\text{OCHC}$ ), 5.43 (5H, s,  $\text{CpH}$ );  $\delta_{\text{C}}$  (100 MHz;  $\text{CDCl}_3$ ) -3.5 (3C, s,  $\text{Si}(\text{CH}_3)_3$ ), 20.8 ( $\text{CCH}_3$ ), 50.8 ( $\text{CHCO}_2\text{CH}_3$ ), 52.4 (2C, s,  $\text{C}(\text{CO}_2\text{CH}_3)_2$ ), 56.4 ( $\text{CHCO}_2\text{CH}_3$ ), 74.2 ( $\text{CHSi}$ ), 86.6 ( $\text{CCCH}_3$ ), 87.3 ( $\text{CHCC}$ ), 90.8 ( $\text{CpC}$ ), 99.0 ( $\text{CH}_3\text{CC}$ ), 172.6 ( $\text{CO}_2\text{CH}_3$ ), 174.9 ( $\text{CO}_2\text{CH}_3$ ), 204.5 ( $\text{Co}(\text{CO})_3$ ), 224.4, 226.9 ( $\text{MoCp}(\text{CO})_2$ );  $m/z$  604 ( $\text{M}^+-3\text{CO}$ , 6%), 576 (100), 548 (9). (ii) Second eluting diastereoisomer (Found:  $\text{M}^+-3\text{CO}$ , 603.9871.  $\text{C}_{24}\text{H}_{27}\text{O}_{10}\text{CoMoSi}$  requires  $\text{M}-3\text{CO}$ , 603.9861);  $\nu_{\text{max}}$  (film)/ $\text{cm}^{-1}$  2047, 1979, 1933 ( $\text{C}\equiv\text{O}$ ), 1744 ( $\text{C}=\text{O}$ );  $\delta_{\text{H}}$  (400 MHz;  $\text{CDCl}_3$ ) 0.09 (9H, s,  $\text{Si}(\text{CH}_3)_3$ ), 2.68 (3H, s,  $\text{CCH}_3$ ), 2.92 (1H, dd,  $J$  8.6, 11.2 Hz,  $\text{CHCO}_2\text{CH}_3$ ), 3.25 (1H, t,  $J$  10.6 Hz,  $\text{CHCO}_2\text{CH}_3$ ), 3.68, 3.69 (3H, s,  $\text{CO}_2\text{CH}_3$ ), 3.81 (1H, d,  $J$  10.6 Hz,  $\text{OCHSi}$ ), 5.13 (1H, d,  $J$  8.6 Hz,  $\text{OCHC}$ ), 5.41 (5H, s,  $\text{CpH}$ );  $\delta_{\text{C}}$  (100



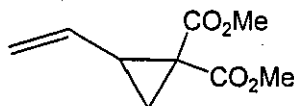
MHz;  $\text{CDCl}_3$ ) -3.5 (3C, s,  $\text{Si}(\text{CH}_3)_3$ ), 21.0 ( $\text{CCH}_3$ ), 50.9 ( $\text{CHCO}_2\text{CH}_3$ ), 52.4, 52.6 ( $\text{CO}_2\text{CH}_3$ ), 55.6 ( $\text{CHCO}_2\text{CH}_3$ ), 74.4 ( $\text{CHSi}$ ), 85.6 ( $\text{CCCH}_3$ ), 87.3 ( $\text{CHCC}$ ), 90.3 ( $\text{CpC}$ ), 100.7 ( $\text{CH}_3\text{CC}$ ), 171.9, 172.4 ( $\text{CO}_2\text{CH}_3$ ), peak absent ( $\text{Co}(\text{CO})_3$ ), 224.5, 226.2 ( $\text{MoCp}(\text{CO})_2$ );  $m/z$  604 ( $\text{M}^+ - 3\text{CO}$ , 6%), 576 (100), 548 (11).

**Cyclopentadienyl molybdenum dicarbonyl cobalt tricarbonyl-1-(tetrahydrofuran-2,3-dicarboxylic acid dimethyl ester-4-trimethylsilyl)propyne (191)**



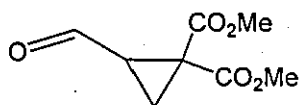
Molybdenum cyclopentadienyl tricarbonyl dimer (0.047 g, 0.09 mmol) was dissolved in dry THF (8 mL) in a flame-dried Schlenk flask under an atmosphere of nitrogen. To this was added K-Selectride (0.23 mL, 0.23 mmol, 1.0 M in THF) and the reaction mixture was stirred for 1.0 h. Dicobalt hexacarbonyl-1-(tetrahydrofuran-2,3-dicarboxylic acid dimethyl ester-4-trimethylsilyl)propyne (0.111 g, 0.19 mmol) in THF (7 mL) was added and the mixture, then refluxed for 2.5 h. The crude product was cooled, concentrated *in vacuo* and purified by flash silica chromatography eluting in petroleum ether-diethyl ether (6:1 v/v) to yield the two separable *title complex* diastereoisomers as red oils ((i) 0.037 g, (ii) 0.027 g, 51%, 1.3:1 d.r.). Spectroscopic data were identical with those reported in the following experiment.

**2-Ethenylcyclopropane-1,1-dicarboxylic acid dimethyl ester (263)<sup>110</sup>**



To a stirred solution of sodium methoxide, prepared from sodium (1.150 g, 50.00 mmol) and methanol (20 mL), was added dimethyl malonate (5.89 mL, 51.50 mmol) followed by a solution of (*E*)-1,4-dibromobutene (5.350 g, 25.00 mmol) in methanol (20 mL). The reaction mixture was refluxed for 2.5 h and then cooled to ambient temperature. The white precipitate was filtered (if present) and the filtrate reduced *in vacuo* to leave an oily residue, which was partitioned between diethyl ether (30 mL) and distilled water (30 mL). The diethyl ether layer was further washed with distilled water (2 x 30 mL), before drying over MgSO<sub>4</sub>, filtering and concentrating *in vacuo* to afford a pale yellow oil, which was purified by flash silica chromatography eluting in petroleum ether-diethyl ether (5:1 v/v) to yield the *title compound* as a colourless oil (6.700 g, 90%) (Found:  $M^+$ , 184.0738. C<sub>9</sub>H<sub>12</sub>O<sub>4</sub> requires  $M$ , 184.0736);  $\nu_{\max}$  (film)/cm<sup>-1</sup> 2955 (sp<sup>3</sup> C-H), 1730 (C=O);  $\delta_H$  (400 MHz; CDCl<sub>3</sub>) 1.58 (1H, dd,  $J$  5.0, 9.0 Hz, CCHH), 1.72 (1H, dd,  $J$  5.0, 7.5 Hz, CCHH), 2.57-2.59 (1H, m, CH<sub>2</sub>CHC), 3.74 (6H, s, (CO<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 5.13 (1H, d,  $J$  10.5 Hz, CHCHH), 5.27 (1H, d,  $J$  17.0 Hz, CHCHH), 5.41 (1H, m, CCHCHCH<sub>2</sub>);  $\delta_C$  (100 MHz; CDCl<sub>3</sub>) 20.9 (CCH<sub>2</sub>), 31.8 (CCHCH), 36.1 (CCH), 52.9, 53.0 (OCH<sub>3</sub>), 119.0 (CCHCHCH<sub>2</sub>), 133.3 (CHCHCH<sub>2</sub>);  $m/z$  184 ( $M^+$ , 15%), 152 (67), 124 (64), 93 (50), 71 (66).

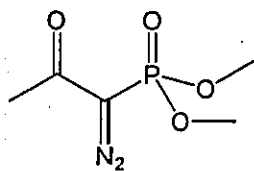
**2-Formyl-cyclopropane-1,1-dicarboxylic acid dimethyl ester (264)<sup>123</sup>**



2-Ethynylcyclopropane-1,1-dicarboxylic acid dimethyl ester (4.300 g, 186.20 mmol) in DCM (35 mL) was added to a flame-dried 3-neck flask fitted with a stopper, cone adapter and gas inlet. Oxygen was bubbled into the reaction mixture for 15 min while cooling to -78°C. Ozone was then generated and bubbled through the reaction mixture at -78°C until a

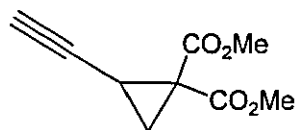
pale blue colour appeared, at which point oxygen was allowed to bubble through the reaction mixture and dimethylsulfide (10 mL) added, stirring for 12.0 h at room temperature. The reaction mixture was then concentrated *in vacuo* and the crude product partitioned between DCM (100 mL) and water (35 mL), washing the DCM fraction with water (2 x 35 mL) before drying, filtering and reducing *in vacuo* to give the *title compound* as a colourless oil (4.000 g, 91%);  $\nu_{\max}$  (film)/ $\text{cm}^{-1}$  2958 ( $\text{sp}^3$  C-H), 1735, 1719 (C=O);  $\delta_{\text{H}}$  (250 MHz;  $\text{CDCl}_3$ ) 1.82 (1H, dd,  $J$  5.0, 8.9 Hz, CHCHH), 2.08 (1H, dd,  $J$  5.0, 6.9 Hz, CHCHH), 2.74-2.78 (1H, m,  $\text{CH}_2\text{CH}$ ), 3.77 (6H, s,  $\text{C}(\text{CO}_2\text{CH}_3)_2$ ), 9.36 (1H, d,  $J$  4.2 Hz, CHO);  $\delta_{\text{C}}$  (100 MHz;  $\text{CDCl}_3$ ) 20.0 ( $\text{CHCH}_2$ ), 35.1 ( $\text{CHCH}_2$ ), 37.9 ( $\text{CCHCH}_2$ ), 53.6, 53.7 ( $\text{OCH}_3$ ), 166.7, 168.7 ( $\text{C}(\text{CO}_2\text{CH}_3)_2$ ), 196.7 (CHO).

#### Dimethyl-1-diazo-2-oxopropylphosphonate (265)<sup>115</sup>



To a cold suspension (0-5°C) of NaH (1.150 g, 28.90 mmol) in benzene (50 mL) and THF (8 mL) was added dimethyl 2-oxopropylphosphonate (4.400 g, 26.30 mmol) in benzene (20 mL) and the suspension stirred for 45 min. Tosyl azide (5.700 g, 28.90 mmol) in benzene (10 mL) was added and the reaction mixture stirred for 2.0 h, whilst warming to room temperature. The mixture was then filtered on a pad of celite and concentrated *in vacuo*, purifying by trituration of the two oils, collecting the *title compound* as a red/orange liquid (5.000 g, 96%);  $\nu_{\max}$  (film)/ $\text{cm}^{-1}$  2125 (C=N<sub>2</sub>), 1670, 1664, 1654, 1648 (C=O);  $\delta_{\text{H}}$  (400 MHz;  $\text{CDCl}_3$ ) 2.28 (3H, s,  $\text{CCH}_3$ ), 3.85, 3.88 (3H, s,  $\text{OCH}_3$ );  $\delta_{\text{C}}$  (100 MHz;  $\text{CDCl}_3$ ) 27.4 ( $\text{CCH}_3$ ), 53.9, 54.0 ( $\text{OCH}_3$ ), 190.2, 190.3 (C=O, C=N).

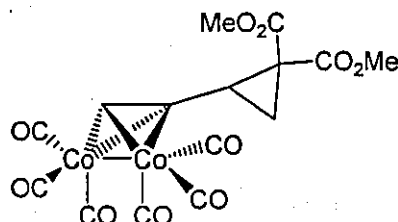
## 2-Ethynylcyclopropane-1,1-dicarboxylic acid dimethyl ester (266)



2-Formylcyclopropane-1,1-dicarboxylic acid dimethyl ester (4.400 g, 23.60 mmol) in dry methanol (35 mL) was placed under a nitrogen atmosphere and dimethyl-1-diazo-2-oxopropylphosphonate (9.500 g, 47.20 mmol) was added, followed by  $K_2CO_3$  (6.500 g, 47.20 mmol). The reaction mixture was stirred for 16.0 h at ambient temperature and then partitioned between diethyl ether (30 mL) and saturated  $NaHCO_3$  (30 mL). The diethyl ether layer was further washed with distilled water (2 x 30 mL), before drying over  $MgSO_4$  and concentrating *in vacuo* to afford a pale yellow oil, which was purified by flash silica chromatography eluting in petroleum ether-diethyl ether (5:1 v/v) to yield the *title compound* as a colourless oil (2.600 g, 60%) (Found:  $M^+$ , 182.0576.  $C_9H_{10}O_4$  requires  $M$ , 182.0579);  $\nu_{max}$  (film)/ $cm^{-1}$  2957 ( $sp^3$  C-H), 2124 ( $C\equiv C$ ), 1736 ( $C=O$ );  $\delta_H$  (250 MHz;  $CDCl_3$ ) 1.58 (1H, dd,  $J$  4.6, 9.3 Hz,  $CHCHH$ ), 1.85 (1H, dd,  $J$  4.6, 7.4 Hz,  $CHCHH$ ), 1.96 (1H, d,  $J$  2.1 Hz,  $CH_2CH$ ), 2.46 (1H, ddd,  $J$  2.2, 7.4, 9.4 Hz,  $CHCCH$ ), 3.74, 3.80 (3H, s,  $OCH_3$ );  $\delta_C$  (100 MHz;  $CDCl_3$ ) 22.3 ( $CHCH_2$ ), 24.2 ( $CHCH_2$ ), 36.2 ( $CCHCH_2$ ), 53.3, 53.5 ( $OCH_3$ ), 69.1 ( $CHCCH$ ), 80.0 ( $CHCCH$ ), 167.1, 169.3 ( $CO_2CH_3$ );  $m/z$  185 ( $M^+$ , 7%), 150 (16), 85 (44), 59 (42), 43 (100).

**Dicobalt hexacarbonyl-2-ethynylcyclopropane-1,1-dicarboxylic acid dimethyl ester**

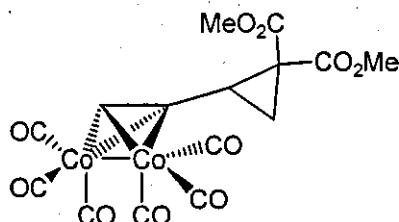
**(176)**



2-Ethynylcyclopropane-1,1-dicarboxylic acid dimethyl ester (0.580 g, 3.20 mmol) was added to a RBF and placed under a nitrogen atmosphere, before dissolving in DCM (25 mL). Cobalt octacarbonyl (1.200 g, 3.50 mmol) was added and the reaction mixture stirred for 1.0 h. The reaction mixture was then filtered on a pad of celite and silica, before concentration *in vacuo* and purification of the residue by flash silica chromatography eluting in petroleum ether-diethyl ether (10:1 v/v) to yield the *title complex* as a deep red solid (1.550 g, 85%) (Found: C, 38.3; H, 2.1%;  $M^+-2CO$ , 411.9036.  $C_{15}H_{10}O_{10}Co_2$  requires C, 38.5; H, 2.2%;  $M-2CO$ , 411.9040);  $\nu_{max}$  (film)/ $cm^{-1}$  2094, 2053, 2020 ( $C\equiv O$ ), 1736 ( $C=O$ );  $\delta_H$  (400 MHz;  $CDCl_3$ ) 1.77 (1H, dd,  $J$  4.6, 7.6 Hz,  $CHCHH$ ), 1.90 (1H, dd,  $J$  4.6, 9.2 Hz,  $CHCHH$ ), 3.34 (1H, ddd,  $J$  0.8, 7.6, 9.2 Hz,  $CH_2CH$ ), 3.77, 3.78 (3H, s,  $OCH_3$ ), 5.68 (1H, d,  $J$  0.8 Hz,  $CHCCH$ );  $\delta_c$  (100 MHz;  $CDCl_3$ ) 27.0 ( $CHCH_2$ ), 31.6 ( $CHCH_2$ ), 41.5 ( $CCH_2$ ), 53.2, 53.4 ( $OCH_3$ ), 69.2 ( $CH_2CH$ ), 90.9 ( $CHCCH$ ), 167.6, 169.5 ( $CO_2CH_3$ ), 199.5 ( $Co(CO)_3$ );  $m/z$  412 ( $M^+-2CO$ , 9%), 384 (24), 356 (100), 328 (63), 300 (42).

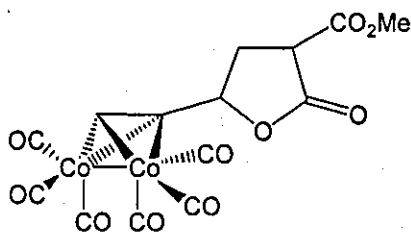
**Dicobalt hexacarbonyl-2-ethynylcyclopropane-1,1-dicarboxylic acid dimethyl ester**

**(176)**



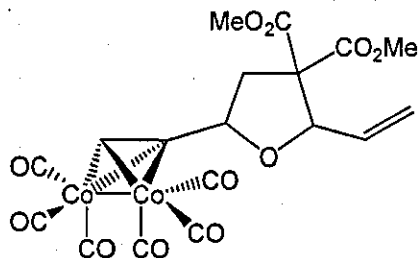
2-Formylcyclopropane-1,1-dicarboxylic acid dimethyl ester (3.620 g, 19.45 mmol) in dry methanol (75 mL) was placed under a nitrogen atmosphere and dimethyl-1-diazo-2-oxopropylphosphonate (7.470 g, 38.89 mmol) was added, followed by  $K_2CO_3$  (5.370 g, 38.89 mmol). The reaction mixture was stirred for 16.0 h at ambient temperature and then partitioned between diethyl ether (50 mL) and saturated  $NaHCO_3$  (50 mL). The diethyl ether layer was further washed with distilled water (2 x 50 mL), before drying over  $MgSO_4$  and concentrating *in vacuo* to afford a yellow oil, which was placed under a nitrogen atmosphere and dissolved in DCM (25 mL). Cobalt octacarbonyl (5.320 g, 15.60 mmol) was added and the reaction mixture stirred for 1.0 h. The crude mixture was then filtered on a pad of celite and silica before concentration *in vacuo* and purification of the residue by flash silica chromatography eluting in petroleum ether-diethyl ether (10:1 v/v) to yield the *title complex* as a deep red solid (4.095 g, 45%). Spectroscopic data were identical with those reported in the previous experiment.

Dicobalt hexacarbonyl-(3-methoxycarbonyltetrahydrofuran-2-on-5-yl)-ethyne (268)



Dicobalt hexacarbonyl-2-ethynylcyclopropane-1,1-dicarboxylic acid dimethyl ester (0.075 g, 0.15 mmol) was added to a flame-dried RBF placed under an atmosphere of nitrogen and dissolved in dry DCM (10 mL). After cooling to 0°C,  $\text{BF}_3 \cdot \text{OEt}_2$  (0.06 mL, 0.46 mmol) was added and the reaction mixture stirred for 1.0 h. The resulting mixture was filtered through a pad of celite and silica, then concentrated *in vacuo* and the residue purified by flash silica chromatography eluting in petroleum ether-diethyl ether (5:1 v/v) to yield the two inseparable *title complex* diastereoisomers as a deep red oil (0.043 g, 59%, 1:1 d.r.) (Found:  $\text{MH}^+$ , 454.8862.  $\text{C}_{14}\text{H}_8\text{O}_{10}\text{Co}_2$  requires  $\text{MH}$ , 454.8860);  $\nu_{\text{max}}$  (film)/ $\text{cm}^{-1}$  2100, 2060, 2020 ( $\text{C}\equiv\text{O}$ ), 1736 ( $\text{C}=\text{O}$ );  $\delta_{\text{H}}$  (400 MHz;  $\text{CDCl}_3$ ) 2.24-2.31 (1H, m,  $\text{CHCHH}$ ), 2.50-2.58 (1H, m,  $\text{CHCHH}$ ), 2.91-2.98 (1H, m,  $\text{CHCHH}$ ), 3.07-3.13 (1H, m,  $\text{CHCHH}$ ), 3.74-3.78 (2H, m, 2 x  $\text{CH}_2\text{CH}$ ), 3.841, 3.844 (3H, s,  $\text{OCH}_3$ ), 5.63 (1H, ddd,  $J$  0.8, 6.4, 9.2 Hz,  $\text{OCHCH}_2$ ), 5.80-5.83 (1H, m,  $\text{OCHCH}_2$ ), 6.14 (1H, d,  $J$  0.8 Hz,  $\text{CCH}$ ), 6.16 (1H, d,  $J$  0.8 Hz,  $\text{CCH}$ );  $\delta_{\text{C}}$  (100 MHz;  $\text{CDCl}_3$ ) 34.6, 34.7 ( $\text{CHCH}_2$ ), 46.9, 47.5 ( $\text{CHCH}_2$ ), 53.2, 53.4 ( $\text{OCH}_3$ ), 72.1, 72.3 ( $\text{CHCCH}$ ), 79.0, 80.0 ( $\text{OCHCH}_2$ ), 90.3, 90.8 ( $\text{CHCCH}$ ), 167.7, 167.9 ( $\text{OCO}$ ), 170.4 ( $\text{CO}_2\text{CH}_3$ ), 198.7 ( $\text{Co}(\text{CO})_3$ );  $m/z$  455 ( $\text{MH}^+$ , 20%), 399 (45), 371 (67), 343 (52).

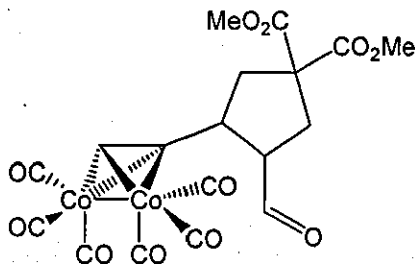
**Dicobalt hexacarbonyl-ethenyl-5-ethynyl-2-tetrahydrofuran-3,3-dicarboxylic acid**  
**dimethyl ester (269)**



Dicobalt hexacarbonyl-2-ethynylcyclopropane-1,1-dicarboxylic acid dimethyl ester (0.065 g, 0.14 mmol) was added to a flame-dried RBF under an atmosphere of nitrogen and dissolved in dry DCM (7 mL). Propenal (0.03 mL, 0.42 mmol) and  $\text{BF}_3 \cdot \text{OEt}_2$  (0.05 mL, 0.42 mmol) were added and the reaction mixture stirred for 0.5 h at reflux. The resulting mixture was filtered through a pad of celite and silica, then concentrated *in vacuo*, and the residue purified by flash silica chromatography eluting in petroleum ether-diethyl ether (5:1 v/v) to yield the two inseparable *title complex* diastereoisomers as a deep red oil (0.020 g, 24%, 1:1 d.r.) (Found:  $\text{M}^+ - 3\text{CO}$ , 439.9350.  $\text{C}_{18}\text{H}_{14}\text{O}_{11}\text{Co}_2$  requires  $\text{M} - 3\text{CO}$  439.9353);  $\nu_{\text{max}}$  (film)/ $\text{cm}^{-1}$  2955 ( $\text{sp}^3 \text{C-H}$ ), 2095, 2053, 2018 ( $\text{C=O}$ ), 1734 ( $\text{C=O}$ );  $\delta_{\text{H}}$  (400 MHz;  $\text{CDCl}_3$ ) 2.15 (1H, dd,  $J$  7.3, 13.3 Hz, CHCHH), 2.65 (1H, dd,  $J$  9.9, 13.3 Hz, CHCHH), 2.75 (1H, dd,  $J$  6.7, 13.3 Hz, CHCHH), 3.21 (1H, dd,  $J$  7.3, 13.3 Hz, CHCHH), 3.67, 3.72, 3.77, 3.81 (3H, s,  $\text{OCH}_3$ ), 4.97-5.07 (3H, m,  $\text{OCHCH}_2$ ,  $\text{OCHCH}_2$ ), 5.18-5.25 (2H, m,  $\text{OCHCH}_2$ ), 5.42 (1H, dt,  $J$  0.8, 5.9 Hz, CHCHCH<sub>2</sub>), 5.46 (1H, dt,  $J$  0.8, 5.9 Hz, CHCHCH<sub>2</sub>), 5.48-5.51 (1H, m,  $\text{OCHCH}_2$ ), 5.82 (1H, dd,  $J$  5.9, 10.4 Hz, OCHC), 5.89 (1H, dd,  $J$  5.9, 10.4 Hz, OCHC), 6.05 (1H, d,  $J$  0.8 Hz, CHCCH), 6.07 (1H, d,  $J$  0.8 Hz, CHCCH);  $\delta_{\text{C}}$  (100 MHz;  $\text{CDCl}_3$ ) 42.0, 42.5 ( $\text{CHCH}_2\text{C}$ ), 52.5, 52.6, 52.9, 53.0 ( $\text{OCH}_3$ ), 58.5, 59.0 ( $\text{CHCH}_2\text{C}$ ), 72.0, 72.3 (CHCCH), 78.0, 78.4 (OCHC), 82.4, 82.9 (OCHCH), 92.9, 95.4 (CHCCH), 117.7, 117.9 (CHCHCH<sub>2</sub>), 132.7, 133.0 (CHCHCH<sub>2</sub>), 169.1, 169.6, 170.7, 171.3 ( $\text{CO}_2\text{CH}_3$ ), 199.3 ( $\text{Co}(\text{CO})_3$ );  $m/z$  468 ( $\text{M}^+ - 2\text{CO}$ , 9%), 440 (59), 412 (100), 384 (46), 356 (49).

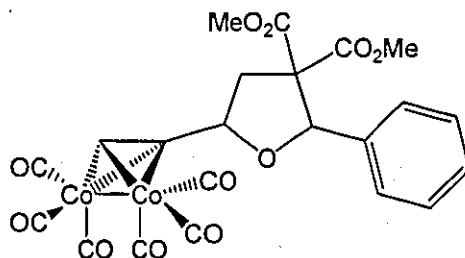


**Dicobalt hexacarbonyl-4-ethynyl-2-formylcyclopentane-1,1-dicarboxylic acid**  
**dimethyl ester (270)**



Also isolated were the two inseparable cyclopentane *title complex* diastereoisomers as a deep red oil (0.017 g, 21%, 2:1 d.r.) (Found:  $M^+-3CO$ , 439.9360.  $C_{18}H_{14}O_{11}Co_2$  requires  $M-3CO$ , 439.9353);  $\nu_{max}$  (film)/ $cm^{-1}$  2094, 2053, 2017 ( $C\equiv O$ ), 1740, 1734, 1730 ( $C=O$ ); Assigned from combined spectrum (i) Major diastereoisomer  $\delta_H$  (250 MHz;  $CDCl_3$ ) 2.20 (1H, dd,  $J$  10.7, 13.4 Hz,  $CHCHHC$ ), 2.61-2.63 (1H, m,  $CHCH_2C$ ), 2.70-2.79 (1H, m,  $CHCH_2C$ ), 2.89 (1H, dd, 7.9, 13.4 Hz,  $CHCHHC$ ), 3.77, 3.78 (3H, s,  $OCH_3$ ), 3.69-3.75 (1H, m,  $CCHCH_2$ ), 6.03 (1H, d,  $J$  1.0 Hz,  $CHCCH$ ), 9.72 (1H, d,  $J$  2.0 Hz,  $CHO$ );  $\delta_c$  (100 MHz;  $CDCl_3$ ) 33.7 ( $CCH_2CH$ ), 41.9 ( $CHCH_2C$ ), 42.0 ( $CHCH_2$ ), 52.1, 52.2 ( $OCH_3$ ), 57.7 ( $CH_2CHC$ ), 58.0 ( $CHCH_2C$ ), 72.4 ( $CHCCH$ ), 100.5 ( $CHCCH$ ), 170.3, 170.7 ( $CO_2CH_3$ ), 198.3 ( $Co(CO)_3$ ), 199.3 ( $CHO$ ). (ii) Minor diastereoisomer  $\delta_H$  (250 MHz;  $CDCl_3$ ) 2.32 (1H, dd,  $J$  12.2, 13.4 Hz,  $CHCHHC$ ), 2.70-2.82 (1H, m,  $CHCHHC$ ,  $CCH_2CH$ ), 3.14-3.18 (1H, m,  $CHCH_2C$ ), 3.76 (6H, s, 2 x  $OCH_3$ ), 3.77-3.86 (1H, m,  $CCHCH_2$ ), 5.98 (1H, d,  $J$  1.1 Hz,  $CHCCH$ ), 9.87 (1H, d,  $J$  2.6 Hz,  $CHO$ );  $\delta_c$  (100 MHz;  $CDCl_3$ ) 33.1 ( $CCH_2CH$ ), 42.2 ( $CHCH_2C$ ), 46.2 ( $CCHCH_2$ ), 52.1, 52.3 ( $OCH_3$ ), 53.3 ( $CH_2CHC$ ), 57.5 ( $CHCH_2C$ ), 72.5 ( $CHCCH$ ), 96.7 ( $CHCCH$ ), 170.7, 171.4 ( $CO_2CH_3$ ), 198.3 ( $Co(CO)_3$ ), 200.7 ( $CHO$ );  $m/z$  468 ( $M^+-2CO$ , 9%), 440 (60), 412 (100), 384 (50), 356 (49).

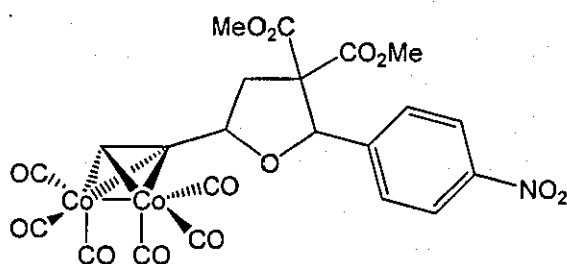
**Dicobalt hexacarbonyl-5-ethynyl-2-phenyltetrahydrofuran-3,3-dicarboxylic acid**  
**dimethyl ester (271)**



Dicobalt hexacarbonyl-2-ethynylcyclopropane-1,1-dicarboxylic acid dimethyl ester (0.045 g, 0.09 mmol) was added to a flame-dried RBF under an atmosphere of nitrogen and dissolved in dry DCM (8 mL). Benzaldehyde (0.02 mL, 0.19 mmol) and  $\text{BF}_3 \cdot \text{OEt}_2$  (0.04 mL, 0.28 mmol) were added and the reaction mixture stirred for 1.0 h. The resulting mixture was filtered through a pad of celite and silica, then concentrated *in vacuo*, and the residue purified by flash silica chromatography eluting in petroleum ether-diethyl ether (5:1 v/v) to yield the two separable *title complex* diastereoisomers as deep red oils ((i) 0.019 g, (ii) 0.019 g, 68%, 1:1 d.r.), (i) First eluting diastereoisomer (Found:  $\text{M}^+ - 2\text{CO}$ , 517.9454.  $\text{C}_{22}\text{H}_{16}\text{O}_{11}\text{Co}_2$  requires  $\text{M} - 2\text{CO}$ , 517.9458);  $\nu_{\text{max}}$  (film)/ $\text{cm}^{-1}$  2094, 2054, 2017 ( $\text{C}\equiv\text{O}$ ), 1739, 1734, 1730 ( $\text{C}=\text{O}$ );  $\delta_{\text{H}}$  (250 MHz;  $\text{CDCl}_3$ ) 2.25 (1H, dd,  $J$  6.7, 13.2 Hz, CHCHH), 3.18 (3H, s,  $\text{OCH}_3$ ), 3.34 (1H, dd,  $J$  7.2, 13.2 Hz, CHCHH), 3.78 (3H, s,  $\text{OCH}_3$ ), 5.76 (1H, app dt,  $J$  0.8, 6.7 Hz, CCHCH<sub>2</sub>), 5.81 (1H, s, OCHC), 6.10 (1H, d,  $J$  0.8 Hz, CHCCH), 7.25-7.35 (3H, m, ArCH), 7.43-7.46 (2H, m, ArCH);  $\delta_{\text{C}}$  (100 MHz;  $\text{CDCl}_3$ ) 43.5 (CHCH<sub>2</sub>C), 52.7, 53.3 ( $\text{OCH}_3$ ), 66.7 (CHCH<sub>2</sub>C), 73.1 (CHCCH), 79.5 (OCHCH<sub>2</sub>), 83.9 (OCHC), 95.5 (CCH), 127.0, 128.3, 128.6 (ArCH), 137.8 (ArC), 169.6, 170.5 ( $\text{CO}_2\text{CH}_3$ ), 199.8 ( $\text{Co}(\text{CO})_3$ );  $m/z$  518 ( $\text{M}^+ - 2\text{CO}$ , 25%), 490 (35), 462 (100), 434 (17), 406 (33). (ii) Second eluting diastereoisomer (Found:  $\text{M}^+ - 2\text{CO}$ , 517.9454.  $\text{C}_{22}\text{H}_{16}\text{O}_{11}\text{Co}_2$  requires  $\text{M} - 2\text{CO}$ , 517.9458);  $\nu_{\text{max}}$  (film)/ $\text{cm}^{-1}$  2094, 2052, 2017 ( $\text{C}\equiv\text{O}$ ), 1739, 1734, 1730 ( $\text{C}=\text{O}$ );  $\delta_{\text{H}}$  (400 MHz;  $\text{CDCl}_3$ ) 2.66 (1H, dd,  $J$  6.4, 13.2 Hz, CHCHH), 2.83 (1H, dd,  $J$  10.0, 13.2 Hz, CHCHH), 3.02, 3.75 (3H, s,  $\text{OCH}_3$ ), 5.00 (1H, ddd,  $J$  0.7, 6.4, 10.0 Hz, OCHCH<sub>2</sub>), 5.67 (1H, s, OCHC), 6.06 (1H, d,  $J$  0.7 Hz, CHCCH), 7.18-7.24 (3H, m, ArCH), 7.37-7.40 (2H, m, ArCH);  $\delta_{\text{C}}$  (100 MHz;  $\text{CDCl}_3$ ) 41.8 (CHCH<sub>2</sub>C), 51.3, 52.0 ( $\text{OCH}_3$ ), 65.0 (CHCH<sub>2</sub>C),

71.0 (CHCCH), 77.0 (OCHCH<sub>2</sub>), 83.4 (OCHC), 91.1 (CCH), 125.8, 126.8, 127.1 (ArCH), 135.8 (ArC), 168.0, 170.2 (CO<sub>2</sub>CH<sub>3</sub>), 199.3 (Co(CO)<sub>3</sub>); *m/z* 518 (M<sup>+</sup>-2CO, 11%), 490 (96), 462 (40), 434 (85), 406 (100).

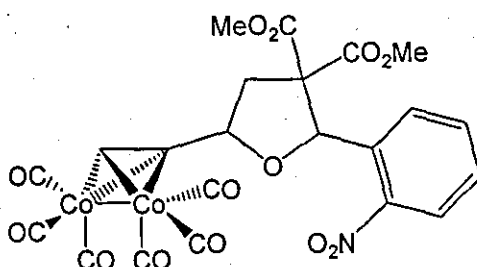
**Dicobalt hexacarbonyl-5-ethynyl-2-(4-nitrophenyl)tetrahydrofuran-3,3-dicarboxylic acid dimethyl ester (273)**



Dicobalt hexacarbonyl-2-ethynylcyclopropane-1,1-dicarboxylic acid dimethyl ester (0.045 g, 0.09 mmol) was added to a flame-dried RBF under an atmosphere of nitrogen and dissolved in dry DCM (8 mL). 4-Nitrobenzaldehyde (0.028 g, 0.18 mmol) and BF<sub>3</sub>·OEt<sub>2</sub> (0.04 mL, 0.28 mmol) were added and the reaction mixture stirred for 1.0 h at reflux. The resulting mixture was filtered through a pad of celite and silica, then concentrated *in vacuo*, and the residue purified by flash silica chromatography eluting in petroleum ether-diethyl ether (5:1 v/v) to yield the two separable *title complex* diastereoisomers as a deep red solid and a deep red oil ((i) 0.021 g, (ii) 0.021 g, 71%, 1:1 d.r.), (i) First eluting diastereoisomer: mp 124-126°C; (Found: C, 42.6; H, 2.3; N, 2.1%; M<sup>+</sup>-2CO, 562.9306. C<sub>22</sub>H<sub>15</sub>O<sub>13</sub>Co<sub>2</sub>N requires C, 42.7; H, 2.4; N, 2.3%; M-2CO, 562.9309); *v*<sub>max</sub> (film)/cm<sup>-1</sup> 2953 (sp<sup>3</sup> C-H), 2095, 2057, 2017 (C≡O), 1740, 1734, 1730 (C=O); δ<sub>H</sub> (250 MHz; CDCl<sub>3</sub>) 2.27 (1H, dd, *J* 7.4, 13.3 Hz, CHCHH), 3.23 (3H, s, OCH<sub>3</sub>), 3.34 (1H, dd, *J* 7.0, 13.3 Hz, CHCHH), 3.81 (3H, s, OCH<sub>3</sub>), 5.78 (1H, app t, *J* 7.0 Hz, CCHCH<sub>2</sub>), 5.85 (1H, s, OCHC), 6.10 (1H, d, *J* 0.7 Hz, CHCCH), 7.69 (2H, d, *J* 8.4 Hz, ArCH), 8.18 (2H, d, *J* 8.4 Hz, ArCH); δ<sub>c</sub> (100 MHz; CDCl<sub>3</sub>) 43.6 (CHCH<sub>2</sub>C), 52.9, 53.6 (OCH<sub>3</sub>), 66.8 (CHCH<sub>2</sub>C), 72.8 (CHCCH), 79.9 (OCHCH<sub>2</sub>), 82.8 (OCHC), 94.7 (CHCCH), 123.5, 128.0 (ArCH), 145.2, 148.1 (ArC), 169.0, 170.1 (CO<sub>2</sub>CH<sub>3</sub>), 199.6 (Co(CO)<sub>3</sub>); *m/z* 563 (M<sup>+</sup>, 25%), 535 (24), 507 (67), 451 (13). (ii) Second eluting diastereoisomer (Found: M<sup>+</sup>-2CO, 562.9320. C<sub>22</sub>H<sub>15</sub>O<sub>13</sub>Co<sub>2</sub>N

requires M-2CO, 562.9309);  $\nu_{\max}$  (film)/cm<sup>-1</sup> 2095, 2052, 2017 (C≡O), 1734, 1706, 1700 (C=O), 1521, 1346 (NO<sub>2</sub>);  $\delta_{\text{H}}$  (400 MHz; CDCl<sub>3</sub>) 2.82 (1H, dd, *J* 6.9, 13.4 Hz, CHCHH), 2.88 (1H, dd, *J* 9.6, 13.4 Hz, CHCHH), 3.16, 3.86 (3H, s, OCH<sub>3</sub>), 5.13 (1H, dd, *J* 6.9, 9.6 Hz, CCHCH<sub>2</sub>), 5.78 (1H, s, OCHC), 6.16 (1H, d, *J* 0.8 Hz, CHCCH), 7.69 (2H, d, *J* 8.9 Hz, ArCH), 8.17 (2H, d, *J* 8.9 Hz, ArCH);  $\delta_{\text{C}}$  (100 MHz; CDCl<sub>3</sub>) 42.7 (CHCH<sub>2</sub>C), 52.4, 53.2 (OCH<sub>3</sub>), 66.1 (CHCH<sub>2</sub>C), 72.0 (CHCCH), 78.6 (OCHCH<sub>2</sub>), 83.2 (OCHC), 91.4 (CHCCH), 123.0, 127.8 (2C, s, ArCH), 147.7, 151.1 (ArC), 168.6, 170.8 (CO<sub>2</sub>CH<sub>3</sub>), 199.3 (Co(CO)<sub>3</sub>); *m/z* 563 (M<sup>+</sup>-2CO, 10%), 535 (15), 507 (100), 451 (17).

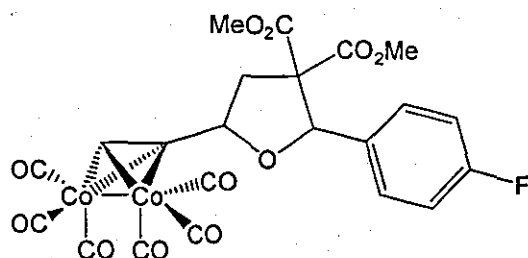
**Dicobalt hexacarbonyl-5-ethynyl-2-(2-nitrophenyl)tetrahydrofuran-3,3-dicarboxylic acid dimethyl ester (274)**



Dicobalt hexacarbonyl-2-ethynylcyclopropane-1,1-dicarboxylic acid dimethyl ester (0.050 g, 0.10 mmol) was added to a flame-dried RBF under an atmosphere of nitrogen and dissolved in dry DCM (8 mL). 2-Nitrobenzaldehyde (0.032 g, 0.20 mmol) and BF<sub>3</sub>·OEt<sub>2</sub> (0.04 mL, 0.31 mmol) were added and the reaction mixture stirred for 1.0 h at reflux. The resulting mixture was filtered through a pad of celite and silica, then concentrated *in vacuo*, and the residue purified by flash silica chromatography eluting in *n*-hexane-diethyl ether (5:1 v/v) to yield the two separable *title complex* diastereoisomers as deep red oils ((i) 0.016 g, (ii) 0.008 g, 30%, 2:1 d.r.), (i) First eluting major diastereoisomer (Found: M<sup>+</sup>-CO, 590.9244. C<sub>22</sub>H<sub>15</sub>O<sub>13</sub>Co<sub>2</sub>N requires M-CO, 590.9258);  $\nu_{\max}$  (film)/cm<sup>-1</sup> 2954 (sp<sup>3</sup> C-H), 2096, 2054, 2025 (C≡O), 1734 (C=O), 1534, 1347 (NO<sub>2</sub>);  $\delta_{\text{H}}$  (400 MHz; CDCl<sub>3</sub>) 2.67 (1H, dd, *J* 5.5, 13.1 Hz, CHCHH), 2.91 (1H, dd, *J* 10.8, 13.1 Hz, CHCHH), 3.15, 3.86 (3H, s, OCH<sub>3</sub>), 5.20 (1H, ddd, *J* 0.8, 5.5, 10.8 Hz, CCHCH<sub>2</sub>), 6.16 (1H, d, *J* 0.8 Hz, CHCCH), 6.44 (1H, s, OCHC), 7.45 (1H, m, ArCH), 7.58 (1H, m, ArCH), 7.75-7.83 (1H, m, ArCH),

7.94-7.97 (1H, m, ArCH);  $\delta_c$  (100 MHz; CDCl<sub>3</sub>) 43.9 (CHCH<sub>2</sub>C), 52.4, 53.3 (OCH<sub>3</sub>), 65.8 (CHCH<sub>2</sub>C), 72.1 (CHCCH), 78.4 (OCHCH<sub>2</sub>), 79.6 (OCHC), 91.1 (CHCCH), 124.3, 128.97, 129.01, 132.7 (ArCH), 148.5, 149.6 (ArC), 168.5, 170.8 (CO<sub>2</sub>CH<sub>3</sub>), 199.2 (Co(CO)<sub>3</sub>);  $m/z$  591 (M<sup>+</sup>-CO, 2%), 563 (3), 535 (3), 507 (2), 451 (75). (ii) Second eluting minor diastereoisomer (Found: M<sup>+</sup>-CO, 590.9247. C<sub>22</sub>H<sub>15</sub>O<sub>13</sub>Co<sub>2</sub>N requires M-CO, 590.9258);  $\nu_{\max}$  (film)/cm<sup>-1</sup> 2095, 2054, 2017 (C≡O), 1734, 1730 (C=O), 1528, 1346 (NO<sub>2</sub>);  $\delta_H$  (400 MHz; CDCl<sub>3</sub>) 2.31 (1H, dd,  $J$  7.5, 13.2 Hz, CHCHH), 3.27 (3H, s, OCH<sub>3</sub>), 3.35 (1H, dd,  $J$  6.9, 13.2 Hz, CHCHH), 3.76 (3H, s, OCH<sub>3</sub>), 5.72 (1H, app dt,  $J$  0.9, 7.5 Hz, CCHCH<sub>2</sub>), 6.10 (1H, d,  $J$  0.9 Hz, CHCCH), 6.48 (1H, s, OCHC), 7.42-7.46 (1H, m, ArCH), 7.57 (1H, m, ArCH), 7.66-7.68 (1H, m, ArCH), 7.82-7.84 (1H, m, ArCH);  $\delta_c$  (100 MHz; CDCl<sub>3</sub>) 43.4 (CHCH<sub>2</sub>C), 52.5, 53.1 (OCH<sub>3</sub>), 66.7 (CHCH<sub>2</sub>C), 72.4 (CHCCH), 78.7 (OCHCH<sub>2</sub>), 79.7 (OCHC), not seen (CHCCH), 124.4, 128.6, 129.0, 132.1 (ArCH), 132.2, 149.2 (ArC), 168.7, 169.2 (CO<sub>2</sub>CH<sub>3</sub>), 199.2 (Co(CO)<sub>3</sub>);  $m/z$  619 (M<sup>+</sup>, 8%), 591 (21), 563 (45), 535 (23) 451 (61).

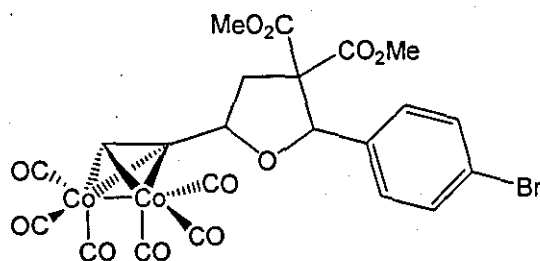
**Dicobalt hexacarbonyl-5-ethynyl-2-(4-fluorophenyl)tetrahydrofuran-3,3-dicarboxylic acid dimethyl ester (275)**



Dicobalt hexacarbonyl-2-ethynylcyclopropane-1,1-dicarboxylic acid dimethyl ester (0.025 g, 0.04 mmol) was added to a flame-dried RBF under an atmosphere of nitrogen and dissolved in dry DCM (5 mL). 4-Fluorobenzaldehyde (0.01 mL, 0.08 mmol) and BF<sub>3</sub>·OEt<sub>2</sub> (0.02 mL, 0.12 mmol) were added and the reaction mixture stirred for 1.0 h at reflux. The resulting mixture was filtered through a pad of celite and silica, then concentrated *in vacuo*, and the residue purified by flash silica chromatography eluting in petroleum ether-diethyl ether (5:1 v/v) to yield the two separable *title complex* diastereoisomers as deep red oils ((i)

0.009, (ii) 0.016 g, 81%, 1:1.7 d.r.), (i) First eluting minor diastereoisomer (Found:  $M^+ - 2CO$ , 535.9374.  $C_{22}H_{15}O_{11}Co_2F$  requires  $M - 2CO$ , 535.9364);  $\nu_{max}$  (film)/ $cm^{-1}$  2095, 2055, 2023 ( $C\equiv O$ ), 1740, 1734, 1730 ( $C=O$ );  $\delta_H$  (400 MHz;  $CDCl_3$ ) 2.17 (1H, dd,  $J$  6.8, 13.2 Hz, CHCHH), 3.09 (3H, s,  $OCH_3$ ), 3.25 (1H, dd,  $J$  7.2, 13.2 Hz, CHCHH), 3.71 (3H, s,  $OCH_3$ ), 5.63 (1H, s, OCHC), 5.67 (1H, app dt,  $J$  0.8, 6.8 Hz, CCHCH<sub>2</sub>), 6.06 (1H, d,  $J$  0.8 Hz, CHCCH), 6.89-6.95 (2H, m, ArCH), 7.36-7.39 (2H, m, ArCH);  $\delta_c$  (100 MHz;  $CDCl_3$ ) 43.0 (CHCH<sub>2</sub>C), 52.4, 52.9 ( $OCH_3$ ), 66.1 (CHCH<sub>2</sub>C), 72.6 (CHCCH), 79.0 (OCHCH<sub>2</sub>), 82.8 (OCHC), 94.9 (CHCCH), 114.8 (2C, d,  $^2J_{C-F}$  21.0 Hz, ArCH), 128.3 (2C, d,  $^3J_{C-F}$  9.0 Hz, ArCH), 133.0 (1C, d,  $^4J_{C-F}$  3.0 Hz, ArC), 162.6 (1C, d,  $^1J_{C-F}$  245.0 Hz, ArC), 169.1, 170.0 ( $CO_2CH_3$ ), 199.3 ( $Co(CO)_3$ );  $m/z$  536 ( $M^+ - 2CO$ , 14%), 508 (15), 480 (100), 452 (25), 452 (25), 424 (28), 365 (20). (ii) Second eluting major diastereoisomer (Found:  $M^+ - 2CO$ , 535.9361.  $C_{22}H_{15}O_{11}Co_2F$  requires  $M - 2CO$ , 535.9364);  $\nu_{max}$  (film)/ $cm^{-1}$  2096, 2054, 2026 ( $C\equiv O$ ), 1734 ( $C=O$ );  $\delta_H$  (400 MHz;  $CDCl_3$ ) 2.67 (1H, dd,  $J$  6.4, 13.4 Hz, CHCHH), 2.80 (1H, dd,  $J$  10.0, 13.4 Hz, CHCHH), 3.16, 3.75 (3H, s,  $OCH_3$ ), 4.99 (1H, ddd,  $J$  0.8, 6.4, 10.0 Hz, OCHCH<sub>2</sub>), 5.70 (1H, s, OCHC), 6.06 (1H, d,  $J$  0.8 Hz, CHCCH), 6.89-6.95 (2H, m, ArCH), 7.36-7.39 (2H, m, ArCH);  $\delta_c$  (100 MHz;  $CDCl_3$ ) 42.7 (CHCH<sub>2</sub>C), 52.3, 53.0 ( $OCH_3$ ), 65.9 (CHCH<sub>2</sub>C), 72.0 (CHCCH), 78.0 (OCHCH<sub>2</sub>), 83.8 (OCHC), 91.9 (CHCCH), 114.7 (2C, d,  $^2J_{C-F}$  21.0 Hz, ArCH), 128.6 (2C, d,  $^3J_{C-F}$  8.0 Hz, ArCH), 132.6 (1C, d,  $^4J_{C-F}$  3.0 Hz, ArC), 162.6 (1C, d,  $^1J_{C-F}$  245.0 Hz, ArC), 169.0, 171.1 ( $CO_2CH_3$ ), 199.3 ( $Co(CO)_3$ );  $m/z$  536 ( $M^+ - 2CO$ , 31%), 508 (45), 480 (100), 452 (16), 424 (20).

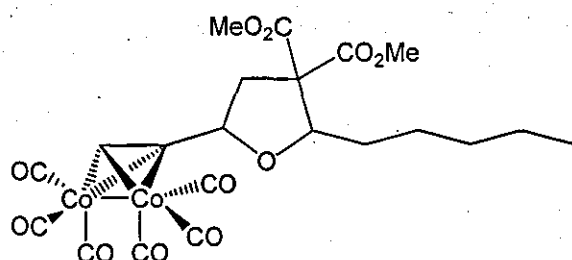
**Dicobalt hexacarbonyl-5-ethynyl-2-(4-bromophenyl)tetrahydrofuran-3,3-dicarboxylic acid dimethyl ester (276)**



Dicobalt hexacarbonyl-2-ethynylcyclopropane-1,1-dicarboxylic acid dimethyl ester (0.050 g, 0.10 mmol) was added to a flame-dried RBF under an atmosphere of nitrogen and dissolved in dry DCM (8 mL). 4-Bromobenzaldehyde (0.038 g, 0.20 mmol) and  $\text{BF}_3 \cdot \text{OEt}_2$  (0.04 mL, 0.29 mmol) were added and the reaction mixture stirred for 1.0 h at reflux. The resulting mixture was filtered through a pad of celite and silica, then concentrated *in vacuo*, and the residue purified by flash silica chromatography eluting in petroleum ether-diethyl ether (5:1 v/v) to yield the two separable *title complex* diastereoisomers as a deep red oil (0.021 g, 0.021 g, 61%, 1:1 d.r.) (i) First eluting diastereoisomer (Found:  $\text{M}^+ - 2\text{CO}$ , 595.8568.  $\text{C}_{22}\text{H}_{15}\text{O}_{11}\text{Co}_2^{79}\text{Br}$  requires  $\text{M} - 2\text{CO}$ , 595.8563);  $\nu_{\text{max}}$  (film)/ $\text{cm}^{-1}$  2094, 2053, 2017 ( $\text{C}\equiv\text{O}$ ), 1740, 1734, 1730 ( $\text{C}=\text{O}$ ), 1072, 1037 ( $\text{C}-\text{O}$ );  $\delta_{\text{H}}$  (400 MHz;  $\text{CDCl}_3$ ) 2.23 (1H, dd,  $J$  6.9, 13.2 Hz,  $\text{CHCHH}$ ), 3.25 (3H, s,  $\text{OCH}_3$ ), 3.31 (1H, dd,  $J$  7.1, 13.2 Hz,  $\text{CHCHH}$ ), 3.78 (3H, s,  $\text{OCH}_3$ ), 5.71-5.75 (2H, m,  $\text{OCHCH}_2$ ,  $\text{OCHC}$ ), 6.09 (1H, d,  $J$  0.7 Hz,  $\text{CHCCH}$ ), 7.34 (2H, d,  $J$  8.6 Hz,  $\text{ArCH}$ ), 7.44 (2H, d,  $J$  8.6 Hz,  $\text{ArCH}$ );  $\delta_{\text{C}}$  (100 MHz;  $\text{CDCl}_3$ ) 43.1 ( $\text{CHCH}_2\text{C}$ ), 52.4, 52.9 ( $\text{OCH}_3$ ), 66.1 ( $\text{CHCH}_2\text{C}$ ), 72.5 ( $\text{CHCCH}$ ), 79.1 ( $\text{OCHCH}_2$ ), 82.9 ( $\text{OCHC}$ ), 94.9 ( $\text{CHCCH}$ ), 122.1 ( $\text{ArC}$ ), 128.3, 131.0 ( $\text{ArCH}$ ), 136.4 ( $\text{ArC}$ ), 168.9, 169.9 ( $\text{CO}_2\text{CH}_3$ ), 199.2 ( $\text{Co}(\text{CO})_3$ );  $m/z$  598 ( $\text{M}^+ - 2\text{CO}$  ( $^{81}\text{Br}$ ), 22%), 595 (21), 569 (27), 567 (25), 541 (100), 539 (98), 485 (30), 483 (30). (ii) Second eluting diastereoisomer (Found:  $\text{M}^+ - 2\text{CO}$ , 595.8550.  $\text{C}_{22}\text{H}_{15}\text{O}_{11}\text{Co}_2^{79}\text{Br}$  requires  $\text{M} - 2\text{CO}$ , 595.8563);  $\nu_{\text{max}}$  (film)/ $\text{cm}^{-1}$  2095, 2054, 2023 ( $\text{C}\equiv\text{O}$ ), 1740, 1734, 1730 ( $\text{C}=\text{O}$ ), 1066, 1035 ( $\text{C}-\text{O}$ );  $\delta_{\text{H}}$  (400 MHz;  $\text{CDCl}_3$ ) 2.74 (1H, dd,  $J$  6.5, 13.2 Hz,  $\text{CHCHH}$ ), 2.86 (1H, dd,  $J$  10.0, 13.2 Hz,  $\text{CHCHH}$ ), 3.17, 3.83 (3H, s,  $\text{OCH}_3$ ), 5.07 (1H, ddd,  $J$  0.8, 6.5, 10.0 Hz,  $\text{CCHCH}_2$ ), 5.67 (1H, s,  $\text{OCHC}$ ), 6.12 (1H, d,  $J$  0.8 Hz,  $\text{CHCCH}$ ), 7.31 (2H, d,  $J$  8.6 Hz,  $\text{ArCH}$ ), 7.43 (2H, d,  $J$  8.6 Hz,  $\text{ArCH}$ );  $\delta_{\text{C}}$

(100 MHz; CDCl<sub>3</sub>) 42.7 (CHCH<sub>2</sub>C), 52.4, 53.1 (OCH<sub>3</sub>), 65.9 (CHCH<sub>2</sub>C), 72.0 (CHCCH), 78.2, (OCHCH<sub>2</sub>), 83.8 (OCHC), 91.9 (CHCCH), 122.2 (ArC), 128.6, 131.0 (ArCH), 135.9 (ArC), 168.9, 171.0 (CO<sub>2</sub>CH<sub>3</sub>), 199.3 (Co(CO)<sub>3</sub>); *m/z* 598 (M<sup>+</sup>-2CO (<sup>81</sup>Br), 5%), 569 (68), 567 (65), 513 (62), 511 (56), 485 (99), 483 (100).

**Dicobalt hexacarbonyl-5-ethynyl-2-pentyltetrahydrofuran-3,3-dicarboxylic acid dimethyl ester (277)**

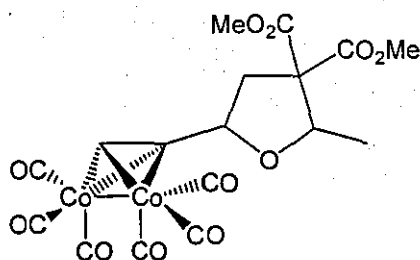


Dicobalt hexacarbonyl-2-ethynylcyclopropane-1,1-dicarboxylic acid dimethyl ester (0.060 g, 0.12 mmol) was added to a flame-dried RBF under an atmosphere of nitrogen and dissolved in dry DCM (10 mL). Hexanal (0.03 mL, 0.25 mmol) and BF<sub>3</sub>·OEt<sub>2</sub> (0.05 mL, 0.37 mmol) were added and the reaction mixture stirred for 1.0 h at reflux. The resulting mixture was filtered through a pad of celite and silica, then concentrated *in vacuo*, and the residue purified by flash silica chromatography eluting in petroleum ether-diethyl ether (5:1 v/v) to yield the two inseparable *title complex* diastereoisomers as a deep red oil (0.064 g, 83%, 1:1 d.r.) (Found: M<sup>+</sup>-2CO, 511.9938. C<sub>21</sub>H<sub>22</sub>O<sub>11</sub>Co<sub>2</sub> requires M-2CO, 511.9928); *v*<sub>max</sub> (film)/cm<sup>-1</sup> 2095, 2055, 2017 (C≡O), 1740, 1734, 1730 (C=O); δ<sub>H</sub> (400 MHz; CDCl<sub>3</sub>) 0.84-0.88 (6H, m, 2 x CHCH<sub>3</sub>), 1.26-1.36 (12H, m, 2 x CH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>), 1.52-1.62 (4H, m, 2 x CH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>), 2.08 (1H, dd, *J* 7.2, 13.2 Hz, CHCHH), 2.60 (1H, dd, *J* 9.6, 13.2 Hz, CHCHH), 2.72 (1H, dd, *J* 6.8, 13.2 Hz, CHCHH), 3.16 (1H, dd, *J* 7.6, 13.2 Hz, CHCHH), 3.74, 3.75, 3.78, 3.79 (3H, s, OCH<sub>3</sub>), 4.45-4.50 (2H, m, 2 x OCHCH<sub>2</sub>), 4.89 (1H, ddd, *J* 0.8, 6.4, 9.6 Hz, OCHC), 5.45 (1H, dt, *J* 0.8, 7.2 Hz, CCHC), 6.03 (1H, d, *J* 0.8 Hz, CHCCH), 6.05 (1H, d, *J* 0.8 Hz, CHCCH); δ<sub>C</sub> (100 MHz; CDCl<sub>3</sub>) 14.0 (2 x CH<sub>2</sub>CH<sub>3</sub>), 22.5 (2 x CH<sub>2</sub>CH<sub>3</sub>), 26.4, 26.5 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 31.6, 31.65, 31.66, 31.8 (CHCH<sub>2</sub>CH<sub>2</sub>), 42.5, 43.0 (CHCH<sub>2</sub>C), 52.4, 52.5, 52.8, 52.9 (OCH<sub>3</sub>), 63.7, 64.0 (CHCH<sub>2</sub>C), 71.6, 72.1



(CHCCH), 77.5, 78.1 (OCHCH<sub>2</sub>), 82.4, 82.9 (OCHC), 93.7, 96.3 (CHCCH), 169.82, 169.84, 169.9, 171.1 (CO<sub>2</sub>CH<sub>3</sub>), 199.4 (Co(CO)<sub>3</sub>); *m/z* 512 (M<sup>+</sup>-2CO, 17%), 584 (17), 456 (53).

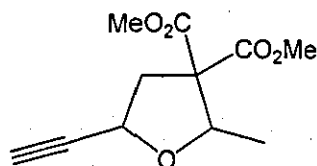
**Dicobalt hexacarbonyl-5-ethynyl-2-methyltetrahydrofuran-3,3-dicarboxylic acid dimethyl ester (278)**



Dicobalt hexacarbonyl-2-ethynylcyclopropane-1,1-dicarboxylic acid dimethyl ester (0.050 g, 0.10 mmol) was added to a flame-dried RBF, placed under an atmosphere of nitrogen and dissolved in dry DCM (10 mL). Acetaldehyde (0.30 mL, 0.20 mmol) and BF<sub>3</sub>·OEt<sub>2</sub> (0.04 mL, 0.30 mmol) were added and the reaction mixture stirred for 1.0 h at reflux. The resulting mixture was filtered through a pad of celite and silica, then concentrated *in vacuo*, and the residue purified by flash silica chromatography eluting in petroleum ether-diethyl ether (5:1 v/v) to yield the two inseparable *title complex* diastereoisomers as a deep red oil (0.036 g, 65%, 1:1 d.r.) (Found: M<sup>+</sup>-2CO, 455.9306. C<sub>17</sub>H<sub>14</sub>O<sub>11</sub>Co<sub>2</sub> requires M-2CO, 455.9302); *v*<sub>max</sub> (film)/cm<sup>-1</sup> 2094, 2053, 2017 (C≡O), 1740, 1734, 1730 (C=O); δ<sub>H</sub> (250 MHz; CDCl<sub>3</sub>) 1.27 (3H, d, *J* 6.5 Hz, CHCH<sub>3</sub>), 1.31 (3H, d, *J* 6.5 Hz, CHCH<sub>3</sub>), 2.12 (1H, dd, *J* 7.2, 13.4 Hz, CHCHH), 2.65 (1H, dd, *J* 9.5, 13.4 Hz, CHCHH), 2.74 (1H, dd, *J* 6.7, 13.4 Hz, CHCHH), 3.17 (1H, dd, *J* 7.6, 13.4 Hz, CHCHH), 3.758, 3.761, 3.79, 3.80 (3H, s, OCH<sub>3</sub>), 4.64 (1H, q, *J* 6.5 Hz, OCHCH<sub>3</sub>), 4.66 (1H, q, *J* 6.5 Hz, OCHCH<sub>3</sub>), 4.93 (1H, ddd, *J* 0.9, 6.5, 9.3 Hz, CCHCH<sub>2</sub>), 5.45 (1H, dt, *J* 1.0, 8.1 Hz, CCHCH<sub>2</sub>), 6.05 (1H, d, *J* 0.9 Hz, CHCCH), 6.06 (1H, d, *J* 1.0 Hz, CHCCH); δ<sub>c</sub> (100 MHz; CDCl<sub>3</sub>) 16.3, 17.0 (CHCH<sub>3</sub>), 42.1, 42.7 (CHCH<sub>2</sub>), 52.6, 52.7, 52.8, 53.0 (OCH<sub>3</sub>), 63.8, 64.0 (CHCH<sub>2</sub>C), 72.0, 72.4 (CHCCH), 77.5, 77.8 (OCHCH<sub>2</sub>), 78.1, 78.9 (OCHC), 93.5, 96.0 (CHCCH), 169.6,

169.69, 169.74, 171.1 ( $\text{CO}_2\text{CH}_3$ ), 199.4 ( $\text{Co}(\text{CO})_3$ );  $m/z$  456 ( $\text{M}^+ - 2\text{CO}$ , 100%), 428 (84), 400 (100), 372 (37), 344 (38).

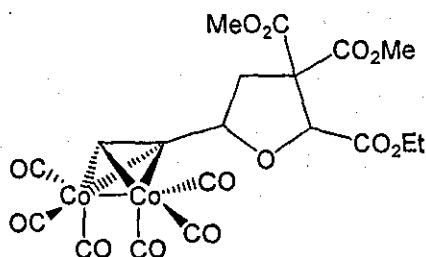
**5-Ethynyl-2-methyltetrahydrofuran-3,3-dicarboxylic acid dimethyl ester (296)**



Dicobalt hexacarbonyl-5-ethynyl-2-methyltetrahydrofuran-3,3-dicarboxylic acid dimethyl ester (0.075 g, 0.15 mmol) in acetone (10 mL) was added to a RBF and cooled to  $-78^\circ\text{C}$ . Triethylamine (0.10 mL) and ceric ammonium nitrate (0.400 g, 0.73 mmol) were added and the reaction mixture stirred for 18.0 h, warming to ambient temperature. The resulting mixture was filtered through a pad of celite, then silica and concentrated *in vacuo*, and the residue purified by flash silica chromatography eluting in petroleum ether-diethyl ether (4:1 v/v) to yield the two separable *title complex* diastereoisomers as colourless oils ((i) 0.014 g, (ii) 0.014 g, 85%, 1:1 d.r.), (i) First eluting diastereoisomer (Found:  $\text{MH}^+$ , 226.0842.  $\text{C}_{11}\text{H}_{14}\text{O}_5$  requires  $\text{MH}$ , 226.0841);  $\nu_{\text{max}}$  (film)/ $\text{cm}^{-1}$  3280 ( $\text{sp}^3 \text{C-H}$ ), 1739, 1734, 1730 ( $\text{C=O}$ ), 1074 ( $\text{C-O}$ );  $\delta_{\text{H}}$  (250 MHz;  $\text{CDCl}_3$ ) 1.29 (3H, d,  $J$  6.3 Hz,  $\text{CHCH}_3$ ), 2.40-2.48 (1H, m,  $\text{CHCHH}$ ), 2.48 (1H, d,  $J$  2.0 Hz,  $\text{CCH}$ ), 3.05 (1H, dd,  $J$  8.0, 13.3 Hz,  $\text{CHCHH}$ ), 3.76, 3.78 (3H, s,  $\text{OCH}_3$ ), 4.73 (1H, q,  $J$  6.3 Hz,  $\text{OCHCH}_3$ ), 4.88-4.94 (1H, m,  $\text{CCHCH}_2$ );  $\delta_{\text{C}}$  (100 MHz;  $\text{CDCl}_3$ ) 16.1 ( $\text{CHCH}_3$ ), 41.1 ( $\text{CHCH}_2$ ), 53.1, 53.3 ( $\text{OCH}_3$ ), 63.1 ( $\text{C}(\text{CO}_2\text{CH}_3)_2$ ), 66.9 ( $\text{CHCH}_2$ ), 74.7 ( $\text{CCH}$ ), 78.6 ( $\text{OCHC}$ ), 82.0 ( $\text{CHCCH}$ ) 169.7, 170.2 ( $\text{CO}_2\text{CH}_3$ );  $m/z$  226 ( $\text{M}^+$ , 4%), 201 (34), 159 (30), 141 (66), 127 (38). (ii) Second eluting diastereoisomer (Found:  $\text{M}^+$ , 225.0762.  $\text{C}_{11}\text{H}_{14}\text{O}_5$  requires  $\text{M}$ , 225.0741);  $\nu_{\text{max}}$  (film)/ $\text{cm}^{-1}$  3275 ( $\text{sp C-H}$ ), 2953 ( $\text{sp}^3 \text{C-H}$ ), 1734 ( $\text{C=O}$ ), 1109 ( $\text{C-O}$ );  $\delta_{\text{H}}$  (400 MHz;  $\text{CDCl}_3$ ) 1.31 (3H, d,  $J$  6.4 Hz,  $\text{CHCH}_3$ ), 2.67 (1H, dd,  $J$  7.2, 13.5 Hz,  $\text{CHCHH}$ ), 2.88 (1H, dd,  $J$  9.0, 13.5 Hz,  $\text{CHCHH}$ ), 3.77, 3.78 (3H, s,  $\text{OCH}_3$ ), 4.48-4.53 (2H, m,  $\text{OCHCH}_3$ ,  $\text{CCHCH}_2$ );  $\delta_{\text{C}}$  (100 MHz;  $\text{CDCl}_3$ ) 17.1 ( $\text{CHCH}_3$ ), 40.6 ( $\text{CHCH}_2$ ), 52.8, 53.0 ( $\text{OCH}_3$ ), 63.4 ( $\text{C}(\text{CO}_2\text{CH}_3)_2$ ), 66.4

(CHCH<sub>2</sub>), 73.9 (CCH), 79.2 (OCHC), 81.6 (CHCCH) 169.2, 170.4 (CO<sub>2</sub>CH<sub>3</sub>); *m/z* 225 (M<sup>+</sup>, 10%), 195 (7), 182 (30), 174 (49), 159 (76), 151 (100), 142 (44).

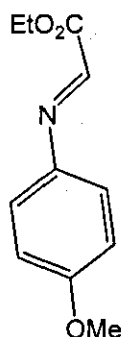
**Dicobalt hexacarbonyl-5-ethynyltetrahydrofuran-2,3,3-tricarboxylic acid 2-ethyl ester 3,3-dimethyl ester (279)**



Dicobalt hexacarbonyl-2-ethynylcyclopropane-1,1-dicarboxylic acid dimethyl ester (0.050 g, 0.11 mmol) was added to a flame-dried RBF under an atmosphere of nitrogen and dissolved in dry DCM (8 mL). Ethyl glyoxylate (0.04 mL, 0.21 mmol) and BF<sub>3</sub>·OEt<sub>2</sub> (0.04 mL, 0.31 mmol) were added, the reaction mixture was heated to reflux and stirred for 1.0 h. The resulting mixture was filtered through a pad of celite and silica, then concentrated *in vacuo*, and the residue purified by flash silica chromatography eluting in petroleum ether-diethyl ether (5:1 v/v) to yield the two inseparable *title complex* diastereoisomers as a deep red oil (0.052 g, 85%, 1.6:1 d.r.) (Found: M<sup>+</sup>-2CO, 513.9366. C<sub>19</sub>H<sub>16</sub>O<sub>13</sub>Co<sub>2</sub> requires M-2CO, 513.9357);  $\nu_{\max}$  (film)/cm<sup>-1</sup> 2096, 2054, 2017 (C≡O), 1751, 1740, 1734 (C=O); Assigned from combined spectrum (i) Major diastereoisomer  $\delta_{\text{H}}$  (400 MHz; CDCl<sub>3</sub>) 1.21 (3H, t, *J* 8.0 Hz, CH<sub>2</sub>CH<sub>3</sub>), 2.32 (1H, dd, *J* 7.4, 13.2 Hz, CHCHH), 3.24 (1H, dd, *J* 7.4, 13.2 Hz, CHCHH), 3.69, 3.75 (3H, s, OCH<sub>3</sub>), 4.08-4.15 (2H, m, CH<sub>2</sub>CH<sub>3</sub>), 5.15 (1H, s, OCHC), 5.58 (1H, m, CCHCH<sub>2</sub>), 6.07 (1H, d, *J* 0.8 Hz, CHCCH);  $\delta_{\text{C}}$  (100 MHz; CDCl<sub>3</sub>) 14.0 (CH<sub>2</sub>CH<sub>3</sub>), 42.2 (CHCH<sub>2</sub>C), 53.3, 53.4 (OCH<sub>3</sub>), 61.5 (CH<sub>2</sub>CH<sub>3</sub>), 64.6 (CHCH<sub>2</sub>C), 72.7 (CHCCH), 79.8 (OCHCH<sub>2</sub>), 81.4 (OCHC), 93.3 (CHCCH), 168.3, 169.2, 169.5 (CO<sub>2</sub>R), 199.1 (Co(CO)<sub>3</sub>); (ii) Minor diastereoisomer  $\delta_{\text{H}}$  (400 MHz; CDCl<sub>3</sub>) 1.20 (3H, t, *J* 7.2 Hz, CH<sub>2</sub>CH<sub>3</sub>), 2.67 (1H, dd, *J* 10.2, 12.9 Hz, CHCHH), 2.84 (1H, dd, *J* 5.9, 12.9 Hz, CHCHH), 3.66, 3.79, (3H, s, OCH<sub>3</sub>), 4.08-4.15 (2H, m, OCH<sub>2</sub>CH<sub>3</sub>), 5.03 (1H, s, OCHC), 5.11 (1H, ddd, *J* 0.8, 5.9, 10.2 Hz, CCHCH<sub>2</sub>), 6.07 (1H, d, *J* 0.8 Hz, CHCCH);  $\delta_{\text{C}}$  (100

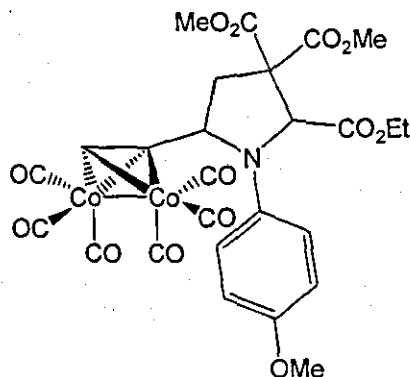
MHz; CDCl<sub>3</sub>) 13.9 (CH<sub>2</sub>CH<sub>3</sub>), 41.4 (CHCH<sub>2</sub>C), 53.1, 53.7 (OCH<sub>3</sub>), 61.5 (CH<sub>2</sub>CH<sub>3</sub>), 64.6 (CHCH<sub>2</sub>C), 72.4 (CHCCH), 80.0 (OCHCH<sub>2</sub>), 81.3 (OCHC), 92.1 (CHCCH), 167.8, 169.1, 169.2 (CO<sub>2</sub>R), 199.1 (Co(CO)<sub>3</sub>); *m/z* 514 (M<sup>+</sup>-2CO, 10%), 486 (42), 458 (100), 430 (18), 402 (59).

**(2-Methoxyphenylimino)acetic acid ethyl ester (286)**



4-Methoxyaniline (1.480 g, 10.00 mmol) was added to a dry RBF containing 4Å mol sieves (15.000 g), and dissolved in diethyl ether (30 mL). Ethyl glyoxylate (2.05 mL, 10.00 mmol, as a 50% solution in toluene) was added and the reaction mixture stirred at ambient temperature for 18.0 h. The mixture was then filtered through a plug of celite and concentrated *in vacuo* to yield the *title compound* as a yellow semi solid (2.210 g, 97%) (Found: M<sup>+</sup>, 207.0900. C<sub>11</sub>H<sub>13</sub>NO<sub>3</sub> requires M, 207.0895); *v*<sub>max</sub> (film)/cm<sup>-1</sup> 2982 (sp<sup>3</sup> C-H), 1729 (C=O), 1646, 1511 (C=N); δ<sub>H</sub> (250 MHz; CDCl<sub>3</sub>) 1.37 (3H, t, *J* 7.0 Hz, CH<sub>2</sub>CH<sub>3</sub>), 3.80 (3H, s, OCH<sub>3</sub>), 4.38 (2H, q, *J* 7.0 Hz, CH<sub>2</sub>CH<sub>3</sub>), 6.90 (2H, d, *J* 8.5 Hz, ArCH), 7.33 (2H, d, *J* 8.5 Hz, ArCH), 7.91 (1H, s, NCHC); δ<sub>c</sub> (100 MHz; CDCl<sub>3</sub>) 14.5 (CH<sub>2</sub>CH<sub>3</sub>), 55.8 (OCH<sub>3</sub>), 62.2 (CH<sub>2</sub>CH<sub>3</sub>), 114.9, 123.9 (ArCH), 141.7 (ArC), 148.3 (NCH), 160.9 (ArC), 163.9 (CO<sub>2</sub>); *m/z* 207 (M<sup>+</sup>, 25%), 149 (9), 134 (100), 107 (20), 92 (15).

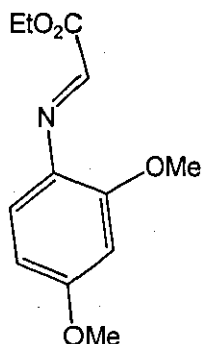
**Dicobalt hexacarbonyl-5-ethynyl-1-(4-methoxyphenyl)pyrrolidine-2,3,3-tricarboxylic acid 2-ethyl ester 3,3-dimethyl ester (287)**



Dicobalt hexacarbonyl-2-ethynylcyclopropane-1,1-dicarboxylic acid dimethyl ester (0.050 g, 0.10 mmol) was added to a flame-dried RBF under an atmosphere of nitrogen and dissolved in dry DCM (10 mL). (4-Methoxyphenylimino)acetic acid ethyl ester (0.040 g, 0.20 mmol) and  $\text{BF}_3 \cdot \text{OEt}_2$  (0.04 mL, 0.31 mmol) were added and the reaction mixture stirred for 1.0 h at reflux. The resulting mixture was filtered through a pad of celite and silica, concentrated *in vacuo*, and the residue purified by flash silica chromatography eluting in petroleum ether-diethyl ether (5:1 v/v) to yield the two inseparable *title complex* diastereoisomers as a deep red oil (0.063 g, 91%, 1:1 d.r.) (Found:  $\text{M}^+ - 2\text{CO}$ , 618.9928.  $\text{C}_{26}\text{H}_{22}\text{O}_{13}\text{Co}_2\text{N}$  requires  $\text{M} - 2\text{CO}$ , 618.9935);  $\nu_{\text{max}}$  (film)/ $\text{cm}^{-1}$  2092, 2053, 2023 ( $\text{C}\equiv\text{O}$ ), 1751, 1743, 1740, 1734, 1730 ( $\text{C}=\text{O}$ );  $\delta_{\text{H}}$  (400 MHz;  $\text{CDCl}_3$ ) 1.02 (3H, t,  $J$  6.8 Hz,  $\text{CH}_2\text{CH}_3$ ), 1.31 (3H, t,  $J$  7.2 Hz,  $\text{CH}_2\text{CH}_3$ ), 2.82 (1H, dd,  $J$  4.4, 14.0 Hz,  $\text{CHCHH}$ ), 3.00 (1H, dd,  $J$  6.0, 12.8 Hz,  $\text{CHCHH}$ ), 3.28 (1H, dd,  $J$  10.2, 12.8 Hz,  $\text{CHCHH}$ ), 3.56 (1H, dd,  $J$  9.4, 14.0 Hz,  $\text{CHCHH}$ ), 3.72, 3.74, 3.76, 3.77, 3.78, 3.86 (3H, s,  $\text{OCH}_3$ ), 3.92-3.96 (2H, m,  $\text{CH}_2\text{CH}_3$ ), 4.20-4.23 (2H, m,  $\text{CH}_2\text{CH}_3$ ), 4.73 (1H, s,  $\text{NCHC}$ ), 4.87 (1H, dd,  $J$  6.4, 10.2 Hz,  $\text{NCHCH}_2$ ), 5.26 (1H, s,  $\text{NCHC}$ ), 5.28 (1H, dd,  $J$  4.4, 9.4 Hz,  $\text{NCHCH}_2$ ), 5.75 (1H, d,  $J$  0.9 Hz,  $\text{CHCCH}$ ), 6.06 (1H, d,  $J$  1.2 Hz,  $\text{CHCCH}$ ), 6.81-6.95 (8H, m,  $\text{ArCH}$ );  $\delta_{\text{C}}$  (100 MHz;  $\text{CDCl}_3$ ) 14.0, 14.1 ( $\text{CH}_2\text{CH}_3$ ), 39.6, 40.3 ( $\text{CHCH}_2\text{C}$ ), 53.0, 53.3, 53.56, 53.63 ( $\text{CO}_2\text{CH}_3$ ), 55.4, 55.5 ( $\text{ArOCH}_3$ ), 58.7, 59.0 ( $\text{CHCH}_2\text{C}$ ), 60.9, 61.5 ( $\text{CH}_2\text{CH}_3$ ), 61.4, 61.8 ( $\text{NCHC}$ ), 70.7, 71.6 ( $\text{NCHCH}_2$ ), 75.5, 76.1 ( $\text{CHCCH}$ ), 94.6, 96.2 ( $\text{CHCCH}$ ), 114.0, 114.3, 116.0, 121.8 ( $\text{ArCH}$ ), 137.3, 140.5, 153.2, 154.9 ( $\text{ArC}$ ), 168.0, 168.6, 169.73, 169.74, 170.0,

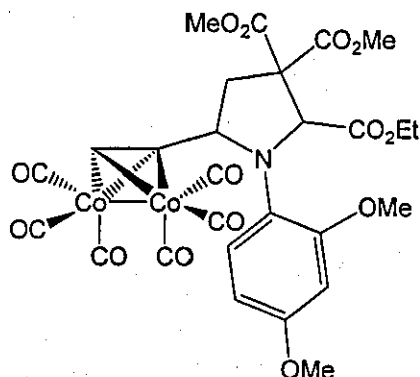
170.7 ( $\text{CO}_2\text{R}$ ), 199.5 ( $\text{Co}(\text{CO})_3$ );  $m/z$  619 ( $\text{M}^+-2\text{CO}$ , 8%), 591 (26), 563 (100), 535 (34), 507 (54).

**(2,4-Dimethoxyphenylimino)acetic acid ethyl ester (288)**



2,4-Dimethoxyaniline (1.530 g, 10.00mmol) was added to a dry RBF containing 4Å mol sieves (15.000 g), and dissolved in diethyl ether (30 mL). Ethyl glyoxylate (2.05 mL, 10.00 mmol, as a 50% solution in toluene) was added and the reaction mixture stirred at ambient temperature for 18.0 h. The mixture was then filtered through a plug of celite and concentrated *in vacuo* to yield the *title compound* as a yellow solid (2.300 g, 96%), mp 44-45°C; (Found:  $\text{M}^+$ , 237.0998.  $\text{C}_{12}\text{H}_{15}\text{NO}_4$  requires  $\text{M}$ , 237.1001);  $\nu_{\text{max}}$  (film)/ $\text{cm}^{-1}$  2981, 2836 ( $\text{sp}^3 \text{C-H}$ ), 1738 ( $\text{C=O}$ ), 1619, 1593 ( $\text{C=N}$ ), 1516 ( $\text{C=C}$ ), 1371, 1284, 1259, 1209, 1159, 1128;  $\delta_{\text{H}}$  (400 MHz;  $\text{CDCl}_3$ ) 1.40 (3H, t,  $J$  7.2 Hz,  $\text{CH}_2\text{CH}_3$ ), 3.82, 3.84 (3H, s,  $\text{OCH}_3$ ), 4.39 (2H, q,  $J$  7.2 Hz,  $\text{CH}_2\text{CH}_3$ ), 6.50-6.52 (2H, m, ArCH), 7.27 (1H, s, ArCH), 8.17 (1H, s, NCHC);  $\delta_{\text{C}}$  (100 MHz;  $\text{CDCl}_3$ ) 14.3 ( $\text{CH}_2\text{CH}_3$ ), 55.6, 55.7 ( $\text{ArOCH}_3$ ), 61.8 ( $\text{CH}_2\text{CH}_3$ ), 99.2, 104.7, 124.7 (ArCH), 130.4 (ArC), 148.6 (NCH), 155.1 ( $\text{CO}_2$ ), 161.5, 164.2 (ArC);  $m/z$  237 ( $\text{M}^+$ , 35%), 164 (100), 153 (22), 138 (26), 122 (14), 107 (17), 77 (13).

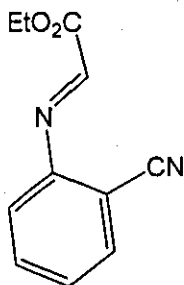
**Dicobalt hexacarbonyl-5-ethynyl-1-(2,4-dimethoxyphenyl)pyrrolidine-2,3,3-tricarboxylic acid 2-ethyl ester 3,3-dimethyl ester (289)**



Dicobalt hexacarbonyl-2-ethynylcyclopropane-1,1-dicarboxylic acid dimethyl ester (0.025 g, 0.05 mmol) was added to a flame-dried RBF under an atmosphere of nitrogen and dissolved in dry DCM (6 mL). (2,4-Dimethoxyphenylimino)acetic acid ethyl ester (0.024 g, 0.10 mmol) and  $\text{BF}_3 \cdot \text{OEt}_2$  (0.02 mL, 0.15 mmol) were added and the reaction mixture stirred for 1.0 h at reflux. The resulting mixture was filtered through a pad of celite and silica, concentrated *in vacuo*, and the residue purified by flash silica chromatography eluting in petroleum ether-diethyl ether (5:1 v/v) to yield the two separable *title complex* diastereoisomers as deep red oils ((i) 0.020 g, (ii) 0.010 g, 78%, 2:1 d.r.), (i) First eluting major diastereoisomer (Found:  $\text{M}^+ - 3\text{CO}$ , 621.0099.  $\text{C}_{27}\text{H}_{25}\text{O}_{14}\text{Co}_2\text{N}$  requires  $\text{M} - 3\text{CO}$ , 621.0092);  $\nu_{\text{max}}$  (film)/ $\text{cm}^{-1}$  2953 ( $\text{sp}^3 \text{C-H}$ ), 2092, 2052, 2023 ( $\text{C}\equiv\text{O}$ ), 1740, 1734 ( $\text{C}=\text{O}$ );  $\delta_{\text{H}}$  (250 MHz;  $\text{CDCl}_3$ ) 1.01 (3H, t,  $J$  7.1 Hz,  $\text{CH}_2\text{CH}_3$ ), 2.83 (1H, dd,  $J$  5.4, 13.6 Hz,  $\text{CHCHH}$ ), 3.43 (1H, dd,  $J$  9.4, 13.6 Hz,  $\text{CHCHH}$ ), 3.72, 3.73, 3.79, 3.84 (3H, s,  $\text{OCH}_3$ ), 3.93 (2H, q,  $J$  7.1 Hz,  $\text{CH}_2\text{CH}_3$ ), 5.33 (1H, dd,  $J$  5.4, 9.4 Hz,  $\text{NCHCH}_2$ ), 5.41 (1H, s,  $\text{NCHC}$ ), 5.62 (1H, s,  $\text{CHCCH}$ ), 6.38-6.42 (2H, m,  $\text{ArCH}$ ), 6.90 (1H, d,  $J$  8.3 Hz,  $\text{ArCH}$ );  $\delta_{\text{C}}$  (100 MHz;  $\text{CDCl}_3$ ) 14.0 ( $\text{CH}_2\text{CH}_3$ ), 38.8 ( $\text{CHCH}_2\text{C}$ ), 53.1, 53.3 ( $\text{CO}_2\text{CH}_3$ ), 55.2, 55.4 ( $\text{ArOCH}_3$ ), 59.0 ( $\text{NCHCH}_2$ ), 60.5 ( $\text{CH}_2\text{CH}_3$ ), 61.5 ( $\text{CHCH}_2\text{C}$ ), 69.2 ( $\text{CHCCH}$ ), 76.1 ( $\text{NCHC}$ ), 96.3 ( $\text{CHCCH}$ ), 99.4 (2C, s,  $\text{ArCH}$ ), 103.0 ( $\text{ArCH}$ ), 125.6, 155.0, 157.0 ( $\text{ArC}$ ), 169.1, 169.7, 170.0 ( $\text{CO}_2\text{R}$ ), 199.3, 199.7 ( $\text{Co}(\text{CO})_3$ );  $m/z$  621 ( $\text{M}^+ - 3\text{CO}$ , 9%), 593 (100), 565 (8), 537 (52). (ii) Second eluting minor diastereoisomer (Found:  $\text{M}^+ - 3\text{CO}$ , 621.0099.  $\text{C}_{27}\text{H}_{25}\text{O}_{14}\text{Co}_2\text{N}$  requires  $\text{M} - 3\text{CO}$ , 621.0092);  $\nu_{\text{max}}$  (film)/ $\text{cm}^{-1}$  2955 ( $\text{sp}^3 \text{C-H}$ ), 2093, 2053,

2023 (C≡O), 1740, 1734 (C=O);  $\delta_H$  (400 MHz; CDCl<sub>3</sub>) 1.29 (3H, t,  $J$  7.2 Hz, CH<sub>2</sub>CH<sub>3</sub>), 2.87 (1H, dd,  $J$  5.9, 12.5 Hz, CHCHH), 3.01 (1H, dd,  $J$  10.7, 12.5 Hz, CHCHH), 3.60, 3.73, 3.78, 3.79 (3H, s, OCH<sub>3</sub>), 4.09-4.26 (2H, m, CH<sub>2</sub>CH<sub>3</sub>), 4.65 (1H, s, NCHC), 4.87 (1H, dd,  $J$  5.9, 10.7 Hz, NCHCH<sub>2</sub>), 5.86 (1H, d,  $J$  0.9 Hz, CHCCH), 6.39-6.44 (2H, m, ArCH), 6.82-6.86 (1H, m, ArCH);  $\delta_C$  (100 MHz; CDCl<sub>3</sub>) 14.3 (CH<sub>2</sub>CH<sub>3</sub>), 38.9 (CHCH<sub>2</sub>C), 53.0, 53.4 (CO<sub>2</sub>CH<sub>3</sub>), 54.7, 55.5 (ArOCH<sub>3</sub>), 59.3 (NCHCH<sub>2</sub>), 61.0 (CH<sub>2</sub>CH<sub>3</sub>), 62.4 (CHCH<sub>2</sub>C), 71.5 (CHCCH), 75.1 (NCHC), 94.7 (CHCCH), 99.7, 103.3, 120.6 (ArCH), 129.1, 153.7, 156.2 (ArC), 168.0, 169.9, 171.6 (CO<sub>2</sub>R), 199.4, 199.7 (Co(CO)<sub>3</sub>);  $m/z$  621 (M<sup>+</sup>-3CO, 3%), 593 (100), 565 (3), 537 (15).

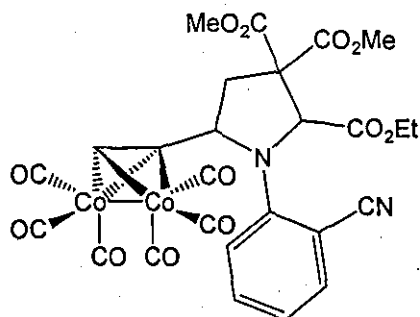
**(2-Cyanophenylimino)acetic acid ethyl ester (290)**



2-Cyanoaniline (1.450 g, 10.00 mmol) was added to a dry RBF containing 4Å mol sieves (15.000 g), and dissolved in diethyl ether (30 mL). Ethyl glyoxylate (2.05 mL, 10.00 mmol, as a 50% solution in toluene) was added and the reaction mixture stirred at ambient temperature for 18.0 h. The mixture was then filtered through a plug of celite and concentrated *in vacuo* to yield the *title compound* as a yellow semi solid (2.150 g, 97%) (Found: M<sup>+</sup>, 202.0743. C<sub>11</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub> requires M, 202.0742);  $\nu_{\max}$  (film)/cm<sup>-1</sup> 2982, 2906 (sp<sup>3</sup> C-H), 2216 (C=N), 1743 (C=O), 1605, 1579 (C=C);  $\delta_H$  (250 MHz; CDCl<sub>3</sub>) 1.23-1.43 (3H, m, CH<sub>2</sub>CH<sub>3</sub>), 4.32 (2H, q,  $J$  7.0 Hz, CH<sub>2</sub>CH<sub>3</sub>), 6.85-6.89 (2H, m, ArCH), 7.43-7.48 (2H, m, ArCH), 7.90 (1H, s, NCHC);  $\delta_C$  (100 MHz; CDCl<sub>3</sub>) 14.4 (CH<sub>2</sub>CH<sub>3</sub>), 62.9 (CH<sub>2</sub>CH<sub>3</sub>), 117.6 (CCN), 125.7, 128.7, 129.5, 133.2 (ArCH), 130.4, 147.6 (ArC), 155.7 (NCH), 162.7 (CO<sub>2</sub>);  $m/z$  202 (M<sup>+</sup>, 4%), 175 (11), 147 (14), 129 (47), 118 (100), 102 (13), 91 (36).



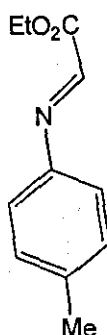
**Dicobalt hexacarbonyl-1-(2-cyanophenyl)-5-ethynylpyrrolidine-2,3,3-tricarboxylic acid 2-ethyl ester 3,3-dimethyl ester (291)**



Dicobalt hexacarbonyl-2-ethynylcyclopropane-1,1-dicarboxylic acid dimethyl ester (0.070 g, 0.14 mmol) was added to a flame-dried RBF under an atmosphere of nitrogen and dissolved in dry DCM (10 mL). (2-Cyanophenylimino)acetic acid ethyl ester (0.059 g, 0.29 mmol) and  $\text{BF}_3 \cdot \text{OEt}_2$  (0.05 mL, 0.43 mmol) were added and the reaction mixture stirred for 1.0 h at reflux. The resulting mixture was filtered through a pad of celite and silica, concentrated *in vacuo*, and the residue purified by flash silica chromatography eluting in petroleum ether-diethyl ether (5:1 v/v) to yield the two inseparable *title complex* diastereoisomers as a deep red oil (0.050 g, 52%, 3:1 d.r.) (Found:  $\text{M}^+ - 3\text{CO}$ , 585.9829.  $\text{C}_{26}\text{H}_{20}\text{O}_{12}\text{Co}_2\text{N}_2$  requires  $\text{M} - 3\text{CO}$ , 585.9833);  $\nu_{\text{max}}$  (film)/ $\text{cm}^{-1}$  2955 ( $\text{sp}^3$  C-H), 2213 ( $\text{C}\equiv\text{N}$ ), 2094, 2055, 2023 ( $\text{C}\equiv\text{O}$ ), 1740, 1734, 1730 ( $\text{C}=\text{O}$ ); Assigned from combined spectrum (i) Major diastereoisomer  $\delta_{\text{H}}$  (250 MHz;  $\text{CDCl}_3$ ) 1.31 (3H, t,  $J$  8.0 Hz,  $\text{CH}_2\text{CH}_3$ ), 2.92-3.00 (1H, m,  $\text{CHCHH}$ ), 3.08 (1H, dd,  $J$  10.0, 12.8 Hz,  $\text{CHCHH}$ ), 3.77, 3.78 (3H, s,  $\text{OCH}_3$ ), 4.15-4.31 (2H, m,  $\text{CH}_2\text{CH}_3$ ), 5.09 (1H, d,  $J$  0.9 Hz,  $\text{NCHC}$ ), 5.30 (1H, dd,  $J$  6.9, 10.0 Hz,  $\text{NCHCH}_2$ ), 6.11 (1H, d,  $J$  0.9 Hz,  $\text{CHCCH}$ ), 6.70-6.76 (1H, m,  $\text{ArCH}$ ), 6.94-6.99 (1H, m,  $\text{ArCH}$ ), 7.29-7.62 (2H, m,  $\text{ArCH}$ );  $\delta_{\text{C}}$  (100 MHz;  $\text{CDCl}_3$ ) 14.0 ( $\text{CH}_2\text{CH}_3$ ), 39.9 ( $\text{CHCH}_2\text{C}$ ), 53.2, 53.78 ( $\text{CO}_2\text{CH}_3$ ), 58.4 ( $\text{NCHCH}_2$ ), 62.2 ( $\text{CH}_2\text{CH}_3$ ), 62.5 ( $\text{CHCH}_2\text{C}$ ), 71.0 ( $\text{CHCCH}$ ), 75.7 ( $\text{NCHC}$ ), 100.5 ( $\text{CHCCH}$ ), 117.6 ( $\text{ArCH}$ ), 119.0 ( $\text{CCN}$ ), 120.6, 133.3, 135.6 ( $\text{ArCH}$ ), 148.5, 149.7 ( $\text{ArC}$ ), 166.9, 169.2, 169.9 ( $\text{CO}_2\text{R}$ ), 199.1, 199.3 ( $\text{Co}(\text{CO})_3$ ). (ii) Minor diastereoisomer  $\delta_{\text{H}}$  (250 MHz;  $\text{CDCl}_3$ ) 0.87 (3H, t,  $J$  6.0 Hz,  $\text{CH}_2\text{CH}_3$ ), 2.32-2.44 (1H, m,  $\text{CHCHH}$ ), 2.52-2.62 (1H, m,  $\text{CHCHH}$ ), 3.79, 3.88 (3H, s,  $\text{OCH}_3$ ), 4.15-4.31 (2H, m,  $\text{CH}_2\text{CH}_3$ ), 4.86-4.95 (1H, m,  $\text{NCHCH}_2$ ), 5.66 (1H, d,  $J$  0.9 Hz,

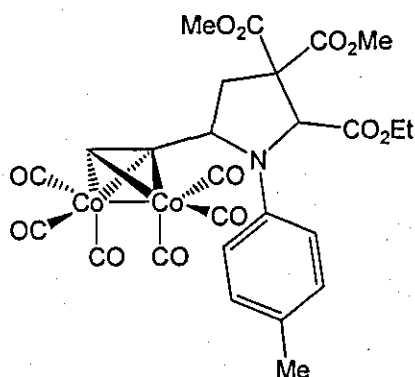
NCHC), 6.02 (1H, d,  $J$  0.9 Hz, CHCCH), 6.70-6.76 (1H, m, ArCH), 6.94-6.99 (1H, m, ArCH), 7.29-7.62 (2H, m, ArCH);  $\delta_c$  (100 MHz; CDCl<sub>3</sub>) 13.8 (CH<sub>2</sub>CH<sub>3</sub>), 36.5 (CHCH<sub>2</sub>C), 53.3, 53.83 (CO<sub>2</sub>CH<sub>3</sub>), 59.1 (NCHCH<sub>2</sub>), 61.4 (CHCH<sub>2</sub>C), 62.2 (CH<sub>2</sub>CH<sub>3</sub>), 70.6 (CHCCH), 73.1 (NCHC), 91.7 (CHCCH), 115.2 (ArCH), 117.1 (CCN), 117.9, 132.3, 134.0 (ArCH), 147.0, 148.2 (ArC), 169.0, 169.2, 169.4 (CO<sub>2</sub>R), 199.1, 199.3 (Co(CO)<sub>3</sub>);  $m/z$  586 (M<sup>+</sup>-3CO, 15%), 558 (47), 530 (44), 502 (73).

**(4-Methylphenylimino)acetic acid ethyl ester (292)**



4-Methylaniline (1.070 g, 10.00 mmol) was added to a dry RBF containing 4 Å mol sieves (15.000 g), and dissolved in diethyl ether (30 mL). Ethyl glyoxylate (2.05 mL, 10.00 mmol, as a 50% solution in toluene) was added and the reaction mixture stirred at ambient temperature for 18.0 h. The mixture was then filtered through a plug of celite and concentrated *in vacuo* to yield the *title compound* as a yellow solid (1.850 g, 97%), mp 65-66°C; (Found: M<sup>+</sup>, 191.0948. C<sub>11</sub>H<sub>13</sub>NO<sub>2</sub> requires M, 191.0946);  $\nu_{\max}$  (film)/cm<sup>-1</sup> 2980 (sp<sup>3</sup> C-H), 1740, 1734, 1718 (C=O), 1624 (C=N);  $\delta_H$  (400 MHz; CDCl<sub>3</sub>) 1.38 (3H, t,  $J$  7.1 Hz, CH<sub>2</sub>CH<sub>3</sub>), 2.34 (3H, s, ArCH<sub>3</sub>), 4.39 (2H, q,  $J$  7.1 Hz, CH<sub>2</sub>CH<sub>3</sub>), 7.17-7.23 (4H, m, ArCH), 7.90 (1H, s, NCHC);  $\delta_c$  (100 MHz; CDCl<sub>3</sub>) 14.5 (CH<sub>2</sub>CH<sub>3</sub>), 21.5 (ArCH<sub>3</sub>), 62.3 (CH<sub>2</sub>CH<sub>3</sub>), 122.0, 130.3 (ArCH), 139.3, 146.5 (ArC), 150.3 (NCH), 163.7 (CO<sub>2</sub>);  $m/z$  191 (M<sup>+</sup>, 26%), 118 (100), 106 (20), 91 (48), 65 (16).

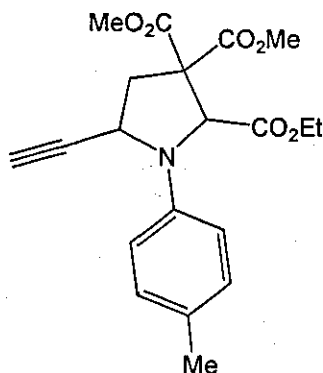
**Dicobalt hexacarbonyl-5-ethynyl-1-(4-methylphenyl)pyrrolidine-2,3,3-tricarboxylic acid 2-ethyl ester 3,3-dimethyl ester (293)**



Dicobalt hexacarbonyl-2-ethynylcyclopropane-1,1-dicarboxylic acid dimethyl ester (0.050 g, 0.10 mmol) was added to a flame-dried RBF under an atmosphere of nitrogen and dissolved in dry DCM (8 mL). (4-Methylphenyl)-acetic acid ethyl ester (0.041 g, 0.21 mmol) and  $\text{BF}_3 \cdot \text{OEt}_2$  (0.04 mL, 0.31 mmol) were added, the reaction mixture heated to reflux and stirred for 1.0 h. The resulting mixture was filtered through a pad of celite and silica, concentrated *in vacuo*, and the residue purified by flash silica chromatography eluting in *n*-hexane-diethyl ether (5:1 v/v) to yield the two inseparable *title complex* diastereoisomers as a deep red oil (0.062 g, 89%, 1:1 d.r.) (Found:  $M^+$  658.9893.  $\text{C}_{26}\text{H}_{23}\text{O}_{12}\text{Co}_2\text{N}$  requires  $M$ , 658.9884);  $\nu_{\text{max}}$  (film)/ $\text{cm}^{-1}$  2093, 2054, 2017 ( $\text{C}\equiv\text{O}$ ), 1751, 1743, 1740, 1730 ( $\text{C}=\text{O}$ );  $\delta_{\text{H}}$  (400 MHz;  $\text{CDCl}_3$ ) 0.94 (3H, t,  $J$  7.0 Hz,  $\text{CH}_2\text{CH}_3$ ), 1.23 (3H, t,  $J$  7.2 Hz,  $\text{CH}_2\text{CH}_3$ ), 2.20 (6H, s, 2 x  $\text{ArCH}_3$ ), 2.73 (1H, dd,  $J$  4.0, 13.6 Hz,  $\text{CHCHH}$ ), 2.94 (1H, dd,  $J$  6.4, 12.9 Hz,  $\text{CHCHH}$ ), 3.20 (1H, dd,  $J$  6.2, 12.9 Hz,  $\text{CHCHH}$ ), 3.50 (1H, dd,  $J$  5.6, 13.6 Hz,  $\text{CHCHH}$ ), 3.63, 3.66, 3.68, 3.78 (3H, s,  $\text{OCH}_3$ ), 3.82-3.91 (2H, m,  $\text{CH}_2\text{CH}_3$ ), 4.10-4.17 (2H, m,  $\text{CH}_2\text{CH}_3$ ), 4.71 (1H, s,  $\text{NCHC}$ ), 4.82 (1H, dd,  $J$  6.4, 10.0 Hz,  $\text{NCHCH}_2$ ), 5.24 (1H, dd,  $J$  4.0, 9.6 Hz,  $\text{NCHCH}_2$ ), 5.28 (1H, s,  $\text{NCHC}$ ), 5.72 (1H, d,  $J$  0.4 Hz,  $\text{CHCCH}$ ), 6.01 (1H, d,  $J$  0.4 Hz,  $\text{CHCCH}$ ), 6.73-6.79 (4H, m,  $\text{ArCH}$ ), 6.97-7.01 (4H, m,  $\text{ArCH}$ );  $\delta_{\text{C}}$  (100 MHz;  $\text{CDCl}_3$ ) 12.9, 13.0 ( $\text{CH}_2\text{CH}_3$ ), 19.4, 19.6 ( $\text{ArCH}_3$ ), 38.7, 39.3 ( $\text{CHCH}_2\text{C}$ ), 52.0, 52.3, 52.5, 52.6 ( $\text{CO}_2\text{CH}_3$ ), 57.6, 57.8 ( $\text{NCHCH}_2$ ), 60.0, 60.5 ( $\text{CH}_2\text{CH}_3$ ), not seen ( $\text{CHCH}_2\text{C}$ ), 69.2, 69.8 ( $\text{NCHC}$ ), 74.7, 75.2 ( $\text{CHCCH}$ ), 93.6, 95.2 ( $\text{CHCCH}$ ), 113.6, 118.6 ( $\text{ArCH}$ ), 127.5, 129.8 ( $\text{ArC}$ ), 128.3, 128.5 ( $\text{ArCH}$ ), 140.6, 143.1 ( $\text{ArC}$ ), 167.0,

167.5, 168.6, 168.7, 168.9, 169.6 (CO<sub>2</sub>R), 198.3 (Co(CO)<sub>3</sub>); *m/z* 659 (M<sup>+</sup>, 3%), 603 (3), 575 (14), 547 (13), 501 (3).

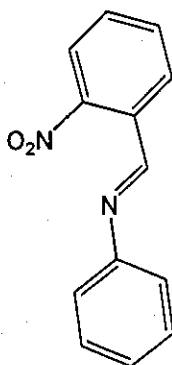
**5-Ethynyl-1-(4-methylphenyl)pyrrolidine-2,3,3-tricarboxylic acid 2-ethyl ester 3,3-dimethyl ester (297)**



Dicobalt hexacarbonyl-5-ethynyl-1-(4-methylphenyl)pyrrolidine-2,3,3-tricarboxylic acid 2-ethyl ester 3,3-dimethyl ester (0.100 g, 0.15 mmol) in acetone (10 mL) was added to a RBF and cooled to -78°C. Triethylamine (0.10 mL) and ceric ammonium nitrate (0.416 g, 0.76 mmol) were added and the reaction mixture stirred for 18.0 h, whilst warming to ambient temperature. The resulting mixture was filtered through a pad of celite and silica, concentrated *in vacuo*, and the residue purified by flash silica chromatography eluting in petroleum ether-diethyl ether (4:1 v/v) to yield the two separable *title complex* diastereoisomers as colourless oils ((i) 0.016 g, (ii) 0.016 g, 57%, 1:1 d.r.), (i) First eluting diastereoisomer (Found: M<sup>+</sup>, 373.1524. C<sub>20</sub>H<sub>23</sub>NO<sub>6</sub> requires M, 373.1525);  $\nu_{\max}$  (film)/cm<sup>-1</sup> 3277 (sp C-H), 1741 (C=O), 1521, 802 (ArC-H);  $\delta_{\text{H}}$  (400 MHz; CDCl<sub>3</sub>) 1.11 (3H, t, *J* 7.0 Hz, CH<sub>2</sub>CH<sub>3</sub>), 2.17 (3H, s, ArCH<sub>3</sub>), 2.20 (1H, d, *J* 1.6 Hz, CCH), 2.81 (1H, d, *J* 13.2 Hz, CHCHH), 3.16 (1H, dd, *J* 9.2, 13.2 Hz, CHCHH), 3.69, 3.72 (3H, s, OCH<sub>3</sub>), 3.91-4.41 (2H, m, CH<sub>2</sub>CH<sub>3</sub>), 4.55-4.58 (1H, m, NCHCH<sub>2</sub>), 5.17 (1H, s, NCHC), 6.58 (2H, d, *J* 8.4 Hz, ArCH), 6.98 (2H, d, *J* 8.4 Hz, ArCH);  $\delta_{\text{C}}$  (100 MHz; CDCl<sub>3</sub>) 14.1 (CH<sub>2</sub>CH<sub>3</sub>), 20.3 (ArCH<sub>3</sub>), 38.0 (CHCH<sub>2</sub>C), 48.2 (NCHCH<sub>2</sub>), 53.3, 53.4 (CO<sub>2</sub>CH<sub>3</sub>), 61.6 (OCH<sub>2</sub>CH<sub>3</sub>), 62.5 (CHCH<sub>2</sub>C), 65.2 (NCHC), 71.9 (CHCCH), 82.8 (CHCCH), 113.3 (ArCH), 127.5 (ArC), 129.7 (ArCH), 141.7 (ArC), 167.7, 168.9, 170.5 (CO<sub>2</sub>R); *m/z* 373 (M<sup>+</sup>, 18%), 354 (6), 314

(7), 301 (22), 300 (100), 241 (14). (ii) Second eluting diastereoisomer  $\nu_{\max}$  (film)/ $\text{cm}^{-1}$  2923 ( $\text{sp}^3$  C-H), 1734, 1718 (C=O), 1517 (ArC-H);  $\delta_{\text{H}}$  (400 MHz;  $\text{CDCl}_3$ ) 1.20 (3H, t,  $J$  7.1 Hz,  $\text{CH}_2\text{CH}_3$ ), 2.33 (4H, s, CCH,  $\text{ArCH}_3$ ), 3.04 (1H, d,  $J$  17.2 Hz, CHCHH), 3.58 (1H, d,  $J$  17.2 Hz, CHCHH), 3.78, 3.85 (3H, s,  $\text{OCH}_3$ ), 4.08-4.18 (3H, m,  $\text{NCHCH}_2$ ,  $\text{CH}_2\text{CH}_3$ ), 5.31 (1H, s, NCHC), 7.18 (2H, d,  $J$  8.3 Hz, ArCH), 7.30 (2H, d,  $J$  8.3 Hz, ArCH);  $\delta_{\text{C}}$  (100 MHz;  $\text{CDCl}_3$ ) 14.0 ( $\text{CH}_2\text{CH}_3$ ), 21.0 ( $\text{ArCH}_3$ ), 38.0 ( $\text{NCHCH}_2$ ), 42.8 ( $\text{CHCH}_2\text{C}$ ), 53.6, 54.0 ( $\text{CO}_2\text{CH}_3$ ), 57.4 ( $\text{CHCH}_2\text{C}$ ), 62.3 (NCHC), 66.6 ( $\text{OCH}_2\text{CH}_3$ ), 79.2 (CHCCH), 88.6 (CHCCH), 123.6 (2C, s, ArCH), 129.8 (2C, s, ArCH), 132.5, 136.7 (ArC), 167.5, 168.5, 170.1 ( $\text{CO}_2\text{R}$ ).

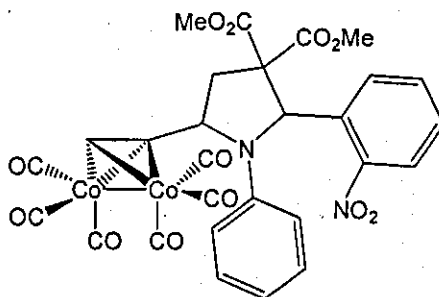
**(2-Nitrobenzylidene)phenylamine (294)**



Aniline (1.000 g, 10.70 mmol) was added to a dry RBF containing 4Å mol sieves (15.000 g), and dissolved in diethyl ether (30 mL). 2-Nitrobenzaldehyde (1.620 g, 10.70 mmol) was added and the reaction mixture stirred at ambient temperature for 18.0 h. The mixture was then filtered through a plug of celite, concentrated *in vacuo* and the residue recrystallised from diethyl ether to yield the *title compound* as a yellow/orange crystalline solid (2.450 g, 94%), mp 65-66°C; (Found:  $M^+$ , 226.0742.  $\text{C}_{13}\text{H}_{10}\text{N}_2\text{O}_2$  requires  $M$ , 226.0742);  $\nu_{\max}$  (film)/ $\text{cm}^{-1}$  1522, 1341 ( $\text{NO}_2$ );  $\delta_{\text{H}}$  (250 MHz;  $\text{CDCl}_3$ ) 7.26-7.31 (3H, m, ArCH), 7.41-7.45 (2H, m, ArCH), 7.60-7.65 (1H, m, ArCH), 7.73-7.77 (ArCH), 8.08 (1H, dd,  $J$  1.4, 7.8 Hz, ArCH), 8.31 (1H, dd,  $J$  1.4, 7.8 Hz, ArCH), 8.90 (1H, s, NCHC);  $\delta_{\text{C}}$  (100 MHz;  $\text{CDCl}_3$ ) 121.2 (2C, s, ArCH), 124.6, 126.9 (ArCH), 129.3 (2C, s, ArCH), 129.6

(ArCH), 131.1 (ArC), 131.2, 133.6 (ArCH), 149.3, 151.0 (ArC), 155.9 (NCH);  $m/z$  226 ( $M^+$ , 53%), 209 (100), 195 (7), 179 (92), 167 (13), 152 (50).

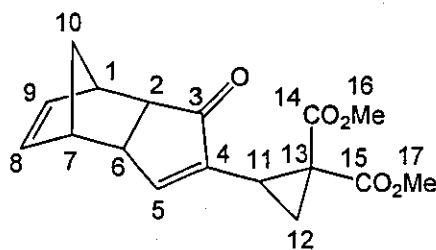
**Dicobalt hexacarbonyl-5-ethynyl-1-phenyl-2-(2-nitrophenyl)pyrrolidine-3,3-dicarboxylic acid dimethyl ester (295)**



Dicobalt hexacarbonyl-2-ethynylcyclopropane-1,1-dicarboxylic acid dimethyl ester (0.100 g, 0.21 mmol) was added to a flame-dried RBF under an atmosphere of nitrogen and dissolved in dry DCM (10 mL). (2-Nitrobenzylidene)phenylamine (0.097 g, 0.42 mmol) and  $\text{BF}_3 \cdot \text{OEt}_2$  (0.08 mL, 0.63 mmol) were added and the reaction mixture stirred for 1.0 h at reflux. The resulting mixture was filtered through a pad of celite and silica, concentrated *in vacuo*, and the residue purified by flash silica chromatography eluting in petroleum ether-diethyl ether (5:1 v/v) to yield the two inseparable *title complex* diastereoisomers as a deep red oil (0.056 g, 32%, 2:1 d.r.), (i) First eluting major diastereoisomer (Found:  $M^+$ , 693.9697.  $\text{C}_{28}\text{H}_{20}\text{O}_{12}\text{Co}_2\text{N}_2$  requires  $M$ , 693.9680);  $\nu_{\text{max}}$  (film)/ $\text{cm}^{-1}$  2953 ( $\text{sp}^3$  C-H), 2093, 2054, 2023 ( $\text{C}\equiv\text{O}$ ), 1740, 1734 ( $\text{C}=\text{O}$ ), 1533, 1350 ( $\text{NO}_2$ ), 1067, 1034 (C-O);  $\delta_{\text{H}}$  (400 MHz;  $\text{CDCl}_3$ ) 2.86 (1H, dd,  $J$  5.8, 13.3 Hz, CHCHH), 3.10 (1H, dd,  $J$  11.3, 13.3 Hz, CHCHH), 3.37, 3.79 (3H, s,  $\text{OCH}_3$ ), 4.92 (1H, dd,  $J$  5.8, 11.3 Hz, NCHCH<sub>2</sub>), 6.24 (1H, d,  $J$  0.9 Hz, CHCCH), 6.55 (1H, s, NCHC), 6.71-6.79 (2H, m, ArCH), 6.86-6.90 (1H, m, ArCH), 7.17-7.21 (2H, m, ArCH), 7.47-7.51 (1H, m, ArCH), 7.63-7.67 (1H, m, ArCH), 7.95-7.98 (1H, m, ArCH), 8.06-8.10 (1H, m, ArCH);  $\delta_{\text{C}}$  (100 MHz;  $\text{CDCl}_3$ ) 41.6 (CHCH<sub>2</sub>C), 52.9, 53.6 ( $\text{CO}_2\text{CH}_3$ ), 58.9 (NCHCH<sub>2</sub>), 63.7 (CHCH<sub>2</sub>C), 68.2 (CHCCH), 76.4 (NCHC), 92.8 (CHCCH), 116.7 (2C, s, ArCH), 120.8, 125.0 (ArCH), 128.8 (2C, s, ArCH), 129.1, 131.2, 132.6 (ArCH), 135.5, 146.9, 148.2 (ArC), 167.4, 170.1 ( $\text{CO}_2\text{CH}_3$ ), 199.1

(Co(CO)<sub>3</sub>); *m/z* 694 (M<sup>+</sup>, 8%), 638 (6), 610 (16), 609 (23), 582 (12), 581 (25), 554 (42), 553 (80) 525 (100). (ii) Second eluting minor diastereoisomer (Found: M<sup>+</sup>, 693.9666. C<sub>28</sub>H<sub>20</sub>O<sub>12</sub>Co<sub>2</sub>N<sub>2</sub> requires M, 693.9680);  $\nu_{\max}$  (film)/cm<sup>-1</sup> 2092, 2053, 2019 (C≡O), 1744, 1740, 1734 (C=O), 1064, 1033 (C-O);  $\delta_{\text{H}}$  (400 MHz; CDCl<sub>3</sub>) 2.64 (1H, dd, *J* 3.0, 14.3 Hz, CHCHH), 3.27 (3H, s, OCH<sub>3</sub>), 3.60 (1H, dd, *J* 8.7, 14.3 Hz, CHCHH), 3.84 (3H, s, OCH<sub>3</sub>), 5.74 (1H, d, *J* 0.8 Hz, CHCCH), 5.82 (1H, dd, *J* 3.0, 8.7 Hz, NCHCH<sub>2</sub>), 6.69-6.73 (1H, m, ArCH), 6.85 (1H, s, NCHC), 6.87-6.89 (2H, m, ArCH), 7.09-7.15 (3H, m, ArCH), 7.29-7.37 (2H, m, ArCH), 7.78-7.80 (1H, m, ArCH);  $\delta_{\text{C}}$  (100 MHz; CDCl<sub>3</sub>) 40.0 (CHCH<sub>2</sub>C), 53.3, peak absent (CO<sub>2</sub>CH<sub>3</sub>), 60.2 (NCHCH<sub>2</sub>), 61.3 (NCHC), 64.9 (CHCH<sub>2</sub>C), 75.6 (CHCCH), 92.8 (CHCCH), 118.0 (2C, s, ArCH), 119.0, 124.7 (ArCH), 128.70 (2C, s, ArCH), 128.74, 129.1, 132.4 (ArCH), 133.2, 142.9, 150.6 (ArC), 168.5, 170.1 (CO<sub>2</sub>CH<sub>3</sub>), 199.1 (Co(CO)<sub>3</sub>); *m/z* (M<sup>+</sup>, 7%), 638 (5), 610 (13), 609 (34), 581 (17), 554 (41), 553 (85), 525 (100).

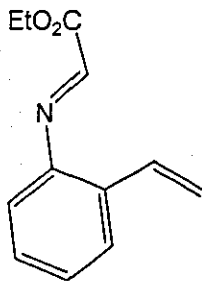
**4-(Cyclopropane-13,13-dicarboxylic acid dimethyl ester)tricyclo[5.2.1.0<sup>2,6</sup>]deca-4,8-dien-3-one (298)**



Dicobalt hexacarbonyl-2-ethynylcyclopropane-1,1-dicarboxylic acid dimethyl ester (0.200 g, 0.04 mmol) was placed in a dry RBF and dissolved in DME (6 mL). Norbornadiene (0.46 mL, 0.85 mmol) was added and the reaction mixture stirred for 2.0 h at 70°C. As no dark red complex spot was present by TLC, the reaction mixture was then filtered on a pad of celite and silica before concentrating *in vacuo* and purification of the residue by flash silica chromatography eluting in petroleum ether-diethyl ether (5:1 v/v) to yield the two inseparable *title complex* diastereoisomers as a yellow oil (0.072 g, 56%, 2:1 d.r.) (Found: M<sup>+</sup>, 302.1147. C<sub>17</sub>H<sub>18</sub>O<sub>5</sub> requires M, 302.1154);  $\nu_{\max}$  (film)/cm<sup>-1</sup> 2952 (sp<sup>3</sup> C-H), 1734,

1700 (C=O), 1432 (C=C), 1287, 1212, 1135 (C-O); Assigned from combined spectrum (i) Major diastereoisomer  $\delta_H$  (400 MHz;  $CDCl_3$ ) 1.18-1.41 (2H, m, *H*-10), 1.64-1.67 (1H, m, *H*-12), 2.03 (1H, dd, *J* 4.8, 8.0 Hz, *H*-12), 2.32-2.35 (1H, m, *H*-11), 2.63-2.84 (1H, m, *H*-2), 2.68 (1H, s, *H*-1), 2.72 (1H, t, *J* 8.7 Hz, *H*-7), 2.91 (1H, br s, *H*-6), 3.64, 3.75 (3H, s, *H*-16/17), 6.18-6.22 (1H, m, *H*-8/9), 6.26-6.30 (1H, m, *H*-8/9), 7.13 (1H, d, *J* 2.4 Hz, *H*-5);  $\delta_C$  (100 MHz;  $CDCl_3$ ) 18.5 (C-12), 23.3 (C-11), 36.2 (C-13), 41.1 (C-10), 43.0 (C-6), 43.8 (C-1), 47.6 (C-7), 52.5 (C-2), 52.8, 52.9 (C-16/17), 137.1, 138.4 (C-8/9), 160.3 (C-5), 167.2, 169.8 (C-14/15), 207.7 (C-3); *m/z* 302 ( $M^+$ , 4%), 270 (37), 238 (51), 204 (100), 183 (34), 176 (50). (ii) Minor diastereoisomer  $\delta_H$  (400 MHz;  $CDCl_3$ ) 1.18-1.41 (2H, m, *H*-10), 1.67-1.71 (1H, m, *H*-12), 1.92 (1H, dd, *J* 4.9, 8.2 Hz, *H*-12), 2.27-2.30 (1H, m, *H*-11), 2.63-2.84 (1H, m, *H*-2), 2.63 (1H, s, *H*-1), 2.80-2.84 (1H, m, *H*-7), 2.91 (1H, br s, *H*-6), 3.63, 3.75 (3H, s, *H*-16/17), 6.18-6.22 (1H, m, *H*-8/9), 6.26-6.30 (1H, m, *H*-8/9), 7.04 (1H, d, *J* 2.7 Hz, *H*-5);  $\delta_C$  (100 MHz;  $CDCl_3$ ) 19.1 (C-12), 22.9 (C-11), 36.9 (C-13), 40.7 (C-10), 43.0 (C-6), 43.8 (C-1), 47.6 (C-7), 52.5 (C-2), 52.8, 52.9 (C-16/17), 137.0, 138.3 (C-8/9), 159.1 (C-5), 167.1, 169.5 (C-14/15), 207.8 (C-3).

**(2-Ethenylphenylimino)acetic acid ethyl ester (299)**

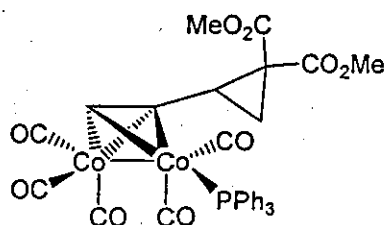


2-Ethynylaniline (0.500 g, 4.30 mmol) was added to a dry RBF containing mol sieves (15.000 g), and dissolved in diethyl ether (30 mL). Ethyl glyoxylate (0.90 mL, 4.30 mmol, as a 50% solution in toluene) was added and the reaction mixture stirred at ambient temperature for 18.0 h. The crude mixture was then filtered through a plug of celite and concentrated *in vacuo* to yield the *title compound* as a pale red oil (0.910 g, 90%) (Found:  $M^+$ , 203.0947.  $C_{12}H_{13}NO_2$  requires  $M$ , 203.0946);  $\nu_{max}$  (film)/ $cm^{-1}$  2980 ( $sp^3$  C-H), 1901



(C=N), 1744, 1715 (C=O);  $\delta_{\text{H}}$  (250 MHz;  $\text{CDCl}_3$ ) 1.38 (3H, t,  $J$  7.2 Hz,  $\text{CH}_2\text{CH}_3$ ), 4.38 (2H, t,  $J$  7.2 Hz,  $\text{CH}_2\text{CH}_3$ ), 5.31 (1H, dd,  $J$  1.2, 11.1 Hz,  $\text{CHCHH}$ ), 5.74 (1H, dd,  $J$  1.2, 17.6 Hz,  $\text{CHCHH}$ ), 6.88-6.90 (1H, m,  $\text{ArCH}$ ), 7.15 (1H, dd,  $J$  11.1, 17.6 Hz,  $\text{CHCHH}$ ), 7.23-7.26 (2H, m,  $\text{ArCH}$ ), 7.57-7.59 (1H, m,  $\text{ArCH}$ ), 7.78 (1H, s,  $\text{NCHC}$ );  $\delta_{\text{C}}$  (100 MHz;  $\text{CDCl}_3$ ) 14.5 ( $\text{CH}_2\text{CH}_3$ ), 62.3 ( $\text{CH}_2\text{CH}_3$ ), 116.2 ( $\text{CHCH}_2$ ), 118.2 ( $\text{CHCH}_2$ ), 126.2, 128.5, 129.2 ( $\text{ArCH}$ ), 132.4, 147.4 ( $\text{ArC}$ ), 151.9 ( $\text{NCH}$ ), 163.3 ( $\text{CO}_2$ );  $m/z$  203 ( $\text{M}^+$ , 9%), 174 (54), 146 (29), 130 (98), 118 (100), 103 (24), 91 (22), 77 (44).

**Dicobalt pentacarbonyl triphenylphosphine-2-ethynylcyclopropane-1,1-dicarboxylic acid dimethyl ester (306)**



Dicobalt hexacarbonyl-2-ethynylcyclopropane-1,1-dicarboxylic acid dimethyl ester (0.125 g, 0.27 mmol) in dry THF (10 mL) was added to a flame-dried flask under an atmosphere of nitrogen and heated to 60°C. To this was added triphenylphosphine (0.058 g, 0.22 mmol) in dry THF (5 mL) and the mixture stirred until no triphenylphosphine was present by TLC, at which time the crude product was cooled, concentrated *in vacuo* and purified by flash silica chromatography eluting in petroleum ether-diethyl ether (4:1 v/v) to yield the two inseparable *title complex* diastereoisomers as a deep red oil (0.122 g, 65%, 3:1 d.r.) (Found:  $\text{M}^+ - 2\text{CO}$ , 646.0011.  $\text{C}_{34}\text{H}_{25}\text{O}_{11}\text{Co}_2\text{P}$  requires  $\text{M} - 2\text{CO}$ , 646.0002);  $\nu_{\text{max}}$  (film)/ $\text{cm}^{-1}$  2060, 2006, 1961 ( $\text{C}\equiv\text{O}$ ), 1729 ( $\text{C}=\text{O}$ ); Assigned from combined spectrum (i) Major diastereoisomer  $\delta_{\text{H}}$  (250 MHz;  $\text{CDCl}_3$ ) 0.87 (1H, dd, 4.7, 7.9 Hz,  $\text{CHCHH}$ ), 1.07 (1H, dd,  $J$  4.7, 9.1 Hz,  $\text{CHCHH}$ ), 3.24 (1H, t,  $J$  8.6 Hz,  $\text{CH}_2\text{CH}$ ), 3.63, 3.69 (3H, s,  $\text{OCH}_3$ ), 4.90 (1H, dd,  $J$  0.7, 2.6 Hz,  $\text{CCH}$ ), 7.35-7.46 (15H, m,  $\text{ArCH}$ );  $\delta_{\text{C}}$  (100 MHz;  $\text{CDCl}_3$ ) 26.2 ( $\text{CHCH}_2$ ), 32.7 ( $\text{CHCH}_2$ ), 39.4 ( $\text{CCH}_2$ ), 52.5, 52.7 ( $\text{OCH}_3$ ), 69.6 ( $\text{CH}_2\text{CH}$ ), 83.3 ( $\text{CHCCH}$ ), 128.6 (2C, d,  $^3J_{\text{C-P}}$  40.0 Hz,  $\text{ArCH}$ ), 130.4 (1C, d,  $^4J_{\text{C-P}}$  8.0 Hz,  $\text{ArC}$ ), 133.1 (2C, d,  $^2J_{\text{C-P}}$  44.0 Hz,

ArCH), 134.5 (1C, d,  $^1J_{C-P}$  164.0 Hz, ArC), 167.2, 169.7 (CO<sub>2</sub>CH<sub>3</sub>), 201.6, 204.4, 205.5 (Co(CO)<sub>3</sub>); (ii) Minor diastereoisomer  $\delta_H$  (250 MHz; CDCl<sub>3</sub>) 0.85-0.90 (1H, m, CHCHH), 1.79 (1H, dd,  $J$  4.5, 9.8 Hz, CHCHH), 3.05 (1H, dd,  $J$  7.5, 10.0 Hz, CH<sub>2</sub>CH), 3.36, 3.68 (3H, s, OCH<sub>3</sub>), 4.89-4.93 (1H, m, CCH), 7.35-7.46 (15H, m, ArCH);  $\delta_c$  (100 MHz; CDCl<sub>3</sub>) 27.9 (CHCH<sub>2</sub>), 31.9 (CHCH<sub>2</sub>), 40.2 (CCH<sub>2</sub>), 52.1, 52.6 (OCH<sub>3</sub>), 68.7 (CH<sub>2</sub>CH), 86.1 (CHCCH), 128.5 (2C, d,  $^3J_{C-P}$  40.0 Hz, ArCH), 130.2 (1C, d,  $^4J_{C-P}$  8.0 Hz, ArC), 133.0 (2C, d,  $^2J_{C-P}$  44.0 Hz, ArCH), 134.4 (1C, d,  $^1J_{C-P}$  164.0 Hz, ArC), 167.1, 169.1 (CO<sub>2</sub>CH<sub>3</sub>), 201.6, 204.4, 205.5 (Co(CO)<sub>3</sub>);  $m/z$  646 (M<sup>+</sup>-2CO, 5%), 618 (90), 590 (20), 562 (100).

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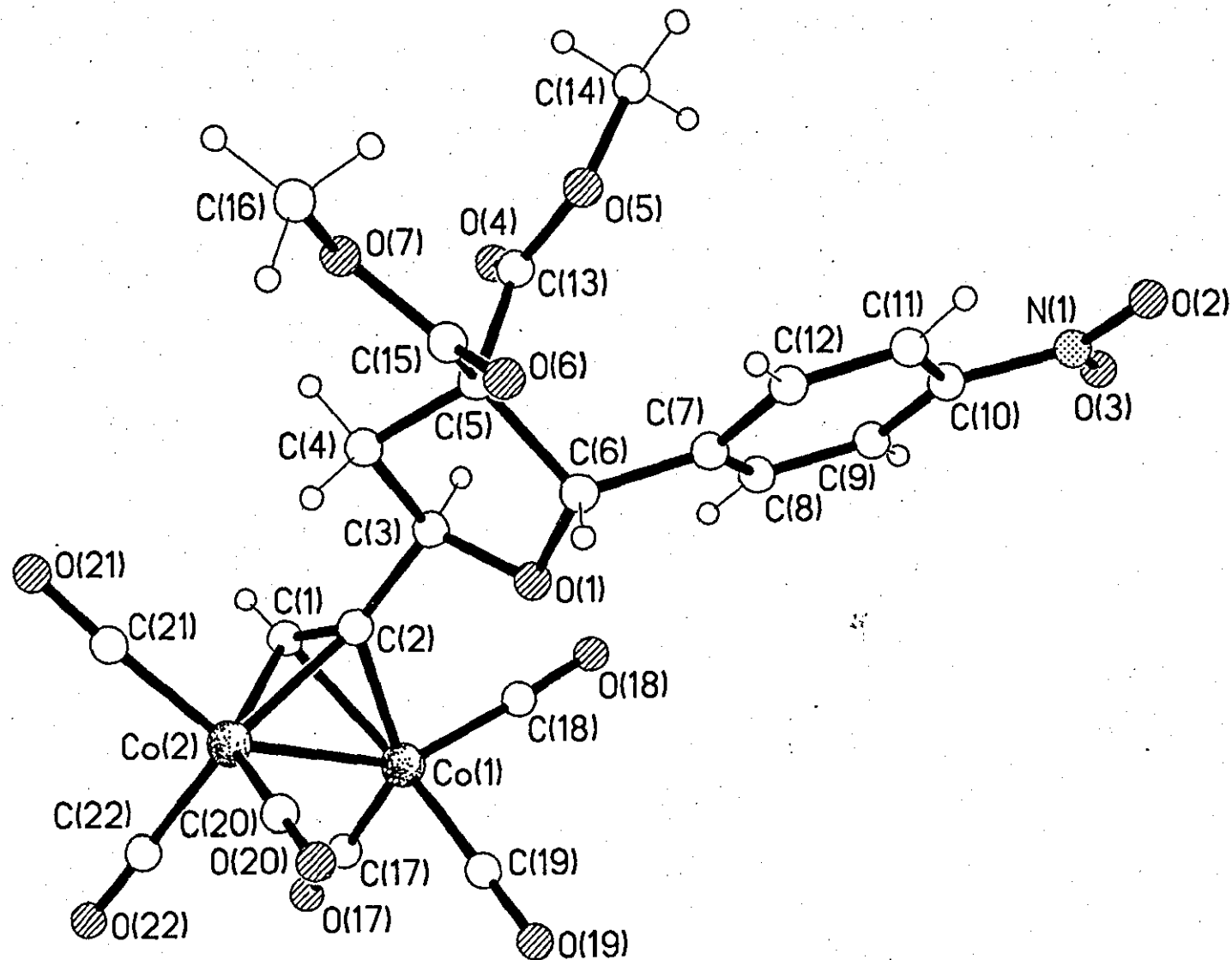
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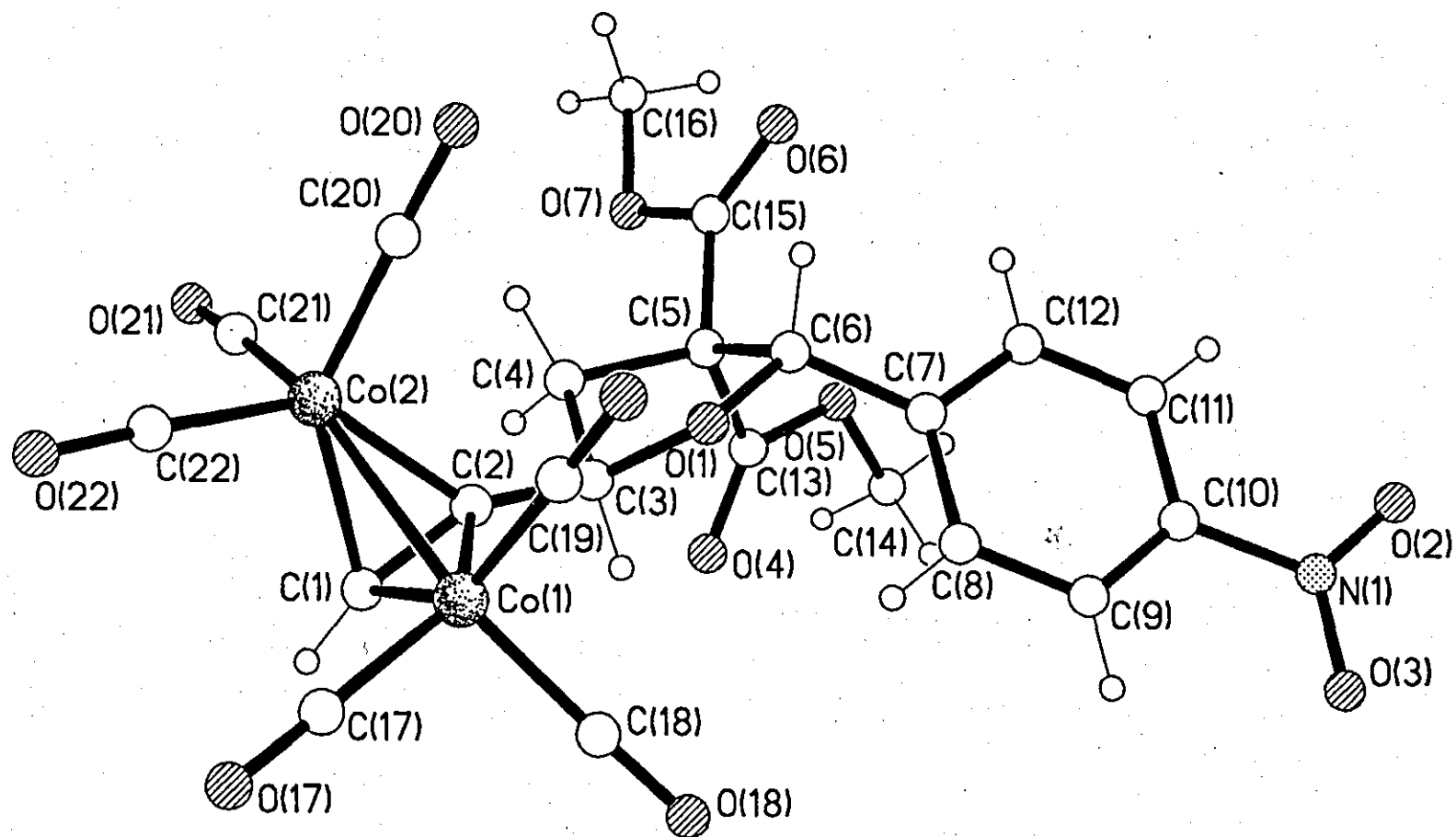


Table 1. Crystal data and structure refinement for sdrc6.

Identification code	sdrc6	
Chemical formula	$C_{22}H_{15}Co_2NO_{13}$	
Formula weight	619.21	
Temperature	150(2) K	
Radiation, wavelength	MoK $\alpha$ , 0.71073 Å	
Crystal system, space group	triclinic, P $\bar{1}$	
Unit cell parameters	a = 6.8834(15) Å	$\alpha = 83.215(4)^\circ$
	b = 8.1890(18) Å	$\beta = 86.122(4)^\circ$
	c = 23.757(5) Å	$\gamma = 67.370(4)^\circ$
Cell volume	1227.0(5) Å <sup>3</sup>	
Z	2	
Calculated density	1.676 g/cm <sup>3</sup>	
Absorption coefficient $\mu$	1.422 mm <sup>-1</sup>	
F(000)	624	
Crystal colour and size	dark red, 0.34 × 0.17 × 0.02 mm <sup>3</sup>	
Reflections for cell refinement	10608 ( $\theta$ range 5.18 to 53.79°)	
Data collection method	Bruker SMART 1000 CCD diffractometer	
	$\omega$ rotation with narrow frames	
$\theta$ range for data collection	1.73 to 22.50°	
Index ranges	h -7 to 7, k -8 to 8, l -24 to 25	
Completeness to $\theta = 22.50^\circ$	99.5 %	
Intensity decay	0%	
Reflections collected	7010	
Independent reflections	3195 ( $R_{int} = 0.0586$ )	
Reflections with $F^2 > 2\sigma$	2122	
Absorption correction	semi-empirical from equivalents	
Min. and max. transmission	0.644 and 0.972	
Structure solution	direct methods	
Refinement method	Full-matrix least-squares on $F^2$	
Weighting parameters a, b	0.0258, 13.7646	
Data / restraints / parameters	3195 / 14 / 349	
Final R indices [ $F^2 > 2\sigma$ ]	$R1 = 0.0769$ , $wR2 = 0.1549$	
R indices (all data)	$R1 = 0.1132$ , $wR2 = 0.1681$	
Goodness-of-fit on $F^2$	1.101	
Extinction coefficient	0.0037(10)	
Largest and mean shift/su	0.000 and 0.000	
Largest diff. peak and hole	0.769 and -0.754 e Å <sup>-3</sup>	

Table 2. Atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ ) for sdr6.  $U_{eq}$  is defined as one third of the trace of the orthogonalized  $U^{ij}$  tensor.

	x	y	z	$U_{eq}$
Co1	0.7670(2)	0.43898(18)	0.37127(6)	0.0281(5)
Co2	0.6619(2)	0.73493(19)	0.40663(6)	0.0264(5)
C1	0.4819(16)	0.6126(13)	0.3869(5)	0.028(3)
C2	0.5616(15)	0.6718(12)	0.3412(5)	0.026(3)
C3	0.4992(16)	0.7472(14)	0.2811(5)	0.032(3)
O1	0.6800(11)	0.7147(9)	0.2448(3)	0.0328(19)
C4	0.3798(15)	0.9493(12)	0.2726(4)	0.024(2)
C5	0.4021(14)	0.9881(12)	0.2072(4)	0.019(2)
C6	0.6293(15)	0.8429(13)	0.1955(4)	0.025(3)
C7	0.6512(14)	0.7571(13)	0.1422(4)	0.021(2)
C8	0.6681(16)	0.5800(13)	0.1431(5)	0.029(3)
C9	0.6947(16)	0.5014(13)	0.0934(4)	0.028(3)
C10	0.7057(15)	0.5964(15)	0.0433(5)	0.030(3)
C11	0.6812(16)	0.7747(14)	0.0398(5)	0.031(3)
C12	0.6570(16)	0.8501(14)	0.0895(4)	0.027(3)
N1	0.7417(14)	0.5106(14)	-0.0099(4)	0.038(2)
O2	0.7621(14)	0.5948(13)	-0.0541(4)	0.060(3)
O3	0.7482(12)	0.3585(11)	-0.0081(3)	0.045(2)
C13	0.2312(15)	0.9620(12)	0.1777(4)	0.017(2)
O4	0.1430(11)	0.8677(9)	0.1982(3)	0.037(2)
O5	0.2069(10)	1.0467(9)	0.1264(3)	0.0276(17)
C14	0.0589(16)	1.0198(15)	0.0923(5)	0.038(3)
C15	0.4028(16)	1.1709(13)	0.1912(4)	0.024(2)
O6	0.5388(11)	1.2110(9)	0.1666(3)	0.0320(18)
O7	0.2172(10)	1.2942(8)	0.2092(3)	0.0250(17)
C16	0.1948(16)	1.4792(12)	0.1955(4)	0.027(2)
C17	0.8077(18)	0.2865(17)	0.4366(6)	0.046(3)
O17	0.8203(15)	0.1991(12)	0.4768(4)	0.070(3)
C18	0.7242(18)	0.3090(15)	0.3226(5)	0.043(3)
O18	0.6909(15)	0.2336(13)	0.2895(5)	0.076(3)
C19	1.025(2)	0.4280(15)	0.3471(5)	0.037(3)
O19	1.1897(13)	0.4225(12)	0.3326(4)	0.051(2)
C20	0.8589(19)	0.8101(15)	0.3768(5)	0.040(3)
O20	0.9868(15)	0.8630(12)	0.3565(5)	0.076(3)
C21	0.455(2)	0.9416(16)	0.4189(5)	0.042(3)
O21	0.3124(15)	1.0684(12)	0.4253(4)	0.072(3)
C22	0.7290(17)	0.6490(14)	0.4782(5)	0.031(3)
O22	0.7707(13)	0.5900(11)	0.5248(4)	0.049(2)

Table 3. Bond lengths [Å] and angles [°] for sdrc6.

Co1–C18	1.771(12)	Co1–C19	1.799(14)
Co1–C17	1.837(14)	Co1–C2	1.971(9)
Co1–C1	1.972(10)	Co1–Co2	2.480(2)
Co2–C20	1.770(13)	Co2–C22	1.782(12)
Co2–C21	1.783(12)	Co2–C2	1.941(11)
Co2–C1	1.975(11)	C1–C2	1.310(14)
C2–C3	1.509(15)	C3–O1	1.420(12)
C3–C4	1.534(14)	O1–C6	1.442(11)
C4–C5	1.557(13)	C5–C15	1.502(13)
C5–C13	1.504(13)	C5–C6	1.589(13)
C6–C7	1.491(14)	C7–C12	1.393(14)
C7–C8	1.407(14)	C8–C9	1.378(14)
C9–C10	1.357(14)	C10–C11	1.397(15)
C10–N1	1.478(14)	C11–C12	1.367(14)
N1–O2	1.218(12)	N1–O3	1.225(12)
C13–O4	1.197(11)	C13–O5	1.315(11)
O5–C14	1.438(12)	C15–O6	1.201(11)
C15–O7	1.367(12)	O7–C16	1.462(11)
C17–O17	1.111(14)	C18–O18	1.140(13)
C19–O19	1.150(13)	C20–O20	1.175(14)
C21–O21	1.140(13)	C22–O22	1.162(12)
C18–Co1–C19	99.4(5)	C18–Co1–C17	100.6(6)
C19–Co1–C17	105.8(5)	C18–Co1–C2	97.7(5)
C19–Co1–C2	107.6(5)	C17–Co1–C2	138.4(5)
C18–Co1–C1	103.5(5)	C19–Co1–C1	141.2(5)
C17–Co1–C1	100.2(5)	C2–Co1–C1	38.8(4)
C18–Co1–Co2	147.7(4)	C19–Co1–Co2	94.5(4)
C17–Co1–Co2	103.4(4)	C2–Co1–Co2	50.1(3)
C1–Co1–Co2	51.1(3)	C20–Co2–C22	107.6(5)
C20–Co2–C21	100.5(5)	C22–Co2–C21	99.2(5)
C20–Co2–C2	102.8(5)	C22–Co2–C2	138.9(5)
C21–Co2–C2	101.7(5)	C20–Co2–C1	141.0(5)
C22–Co2–C1	103.6(5)	C21–Co2–C1	97.1(5)
C2–Co2–C1	39.1(4)	C20–Co2–Co1	102.9(4)
C22–Co2–Co1	94.9(3)	C21–Co2–Co1	147.6(4)
C2–Co2–Co1	51.2(3)	C1–Co2–Co1	51.0(3)
C2–C1–Co1	70.5(6)	C2–C1–Co2	69.1(7)
Co1–C1–Co2	77.9(4)	C1–C2–C3	138.6(10)
C1–C2–Co2	71.9(7)	C3–C2–Co2	138.8(8)
C1–C2–Co1	70.7(6)	C3–C2–Co1	130.7(7)
Co2–C2–Co1	78.7(4)	O1–C3–C2	110.7(8)
O1–C3–C4	104.4(8)	C2–C3–C4	115.2(9)
C3–O1–C6	109.6(7)	C3–C4–C5	101.7(8)
C15–C5–C13	111.3(8)	C15–C5–C4	111.6(8)
C13–C5–C4	110.3(8)	C15–C5–C6	109.7(8)
C13–C5–C6	112.9(8)	C4–C5–C6	100.6(7)
O1–C6–C7	112.0(8)	O1–C6–C5	106.9(8)
C7–C6–C5	114.8(8)	C12–C7–C8	117.5(10)

C12-C7-C6	120.8(9)	C8-C7-C6	121.7(9)
C9-C8-C7	120.8(10)	C10-C9-C8	119.3(10)
C9-C10-C11	122.3(10)	C9-C10-N1	119.5(10)
C11-C10-N1	118.2(10)	C12-C11-C10	117.5(10)
C11-C12-C7	122.5(10)	O2-N1-O3	122.3(10)
O2-N1-C10	118.6(10)	O3-N1-C10	119.1(10)
O4-C13-O5	126.8(9)	O4-C13-C5	122.9(9)
O5-C13-C5	110.1(8)	C13-O5-C14	115.2(8)
O6-C15-O7	122.7(9)	O6-C15-C5	128.2(9)
O7-C15-C5	109.1(9)	C15-O7-C16	115.0(8)
O17-C17-Co1	175.9(11)	O18-C18-Co1	176.3(11)
O19-C19-Co1	178.6(10)	O20-C20-Co2	178.7(11)
O21-C21-Co2	174.6(12)	O22-C22-Co2	178.3(10)

Table 4. Anisotropic displacement parameters ( $\text{\AA}^2$ ) for sdrc6. The anisotropic displacement factor exponent takes the form:  $-2\pi^2[h^2a^{*2}U^{11} + \dots + 2hka^*b^*U^{12}]$

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{23}$	$U^{13}$	$U^{12}$
Co1	0.0267(9)	0.0185(8)	0.0340(10)	-0.0015(7)	-0.0045(7)	-0.0027(7)
Co2	0.0241(9)	0.0238(9)	0.0276(9)	-0.0034(7)	0.0020(7)	-0.0054(7)
C1	0.018(6)	0.014(6)	0.045(7)	0.009(5)	0.005(5)	-0.001(5)
C2	0.015(6)	0.013(5)	0.037(7)	0.001(5)	0.000(5)	0.009(5)
C3	0.022(6)	0.032(7)	0.037(7)	-0.010(5)	0.007(5)	-0.005(5)
O1	0.033(4)	0.026(4)	0.027(4)	0.005(3)	0.002(3)	0.000(3)
C4	0.017(6)	0.018(6)	0.029(6)	0.001(5)	0.010(5)	0.000(5)
C5	0.016(5)	0.011(5)	0.029(6)	0.000(4)	0.000(5)	-0.005(4)
C6	0.017(6)	0.023(6)	0.034(7)	-0.001(5)	-0.001(5)	-0.005(5)
C7	0.010(5)	0.021(6)	0.026(6)	0.000(5)	0.005(4)	0.001(4)
C8	0.034(7)	0.013(6)	0.033(7)	0.004(5)	-0.006(5)	-0.002(5)
C9	0.036(7)	0.015(6)	0.031(7)	0.001(5)	0.002(5)	-0.007(5)
C10	0.018(6)	0.038(7)	0.027(7)	-0.011(6)	0.000(5)	0.000(5)
C11	0.029(6)	0.029(7)	0.029(7)	0.003(5)	-0.006(5)	-0.007(5)
C12	0.031(6)	0.025(6)	0.029(7)	-0.010(5)	0.004(5)	-0.012(5)
N1	0.034(6)	0.042(7)	0.030(6)	-0.006(5)	0.005(5)	-0.007(5)
O2	0.070(7)	0.082(7)	0.030(5)	-0.020(5)	0.008(5)	-0.027(6)
O3	0.046(5)	0.038(5)	0.048(6)	-0.012(4)	-0.004(4)	-0.009(4)
C13	0.022(6)	0.008(5)	0.023(6)	0.000(5)	0.001(5)	-0.008(5)
O4	0.029(4)	0.025(4)	0.050(5)	0.012(4)	-0.014(4)	-0.006(4)
O5	0.029(4)	0.024(4)	0.029(4)	-0.006(3)	-0.002(3)	-0.008(3)
C14	0.023(6)	0.039(7)	0.050(8)	-0.006(6)	-0.002(6)	-0.009(6)
C15	0.019(6)	0.023(6)	0.027(6)	-0.002(5)	-0.006(5)	-0.004(5)
O6	0.029(4)	0.020(4)	0.045(5)	-0.005(4)	0.006(4)	-0.008(3)
O7	0.020(4)	0.016(4)	0.037(4)	-0.006(3)	0.005(3)	-0.004(3)
C16	0.029(4)	0.015(4)	0.031(4)	0.000(3)	-0.002(4)	-0.004(3)
C17	0.036(8)	0.043(8)	0.052(9)	0.003(7)	-0.018(7)	-0.006(6)
O17	0.070(7)	0.051(6)	0.054(6)	0.020(5)	0.007(5)	0.006(5)
C18	0.043(8)	0.026(7)	0.053(9)	-0.012(6)	-0.029(7)	0.000(6)
O18	0.074(7)	0.056(6)	0.098(9)	-0.021(6)	-0.033(6)	-0.014(5)
C19	0.035(8)	0.037(7)	0.027(7)	-0.007(6)	-0.011(6)	0.004(6)
O19	0.033(5)	0.064(6)	0.054(6)	-0.024(5)	0.010(4)	-0.013(5)
C20	0.039(8)	0.034(7)	0.044(8)	-0.003(6)	-0.001(6)	-0.012(6)
O20	0.050(6)	0.043(6)	0.130(10)	0.006(6)	0.015(6)	-0.019(5)
C21	0.051(8)	0.030(7)	0.036(7)	0.001(6)	0.009(6)	-0.008(7)
O21	0.068(7)	0.039(6)	0.079(7)	-0.015(5)	0.001(5)	0.016(5)
C22	0.035(7)	0.023(6)	0.036(8)	-0.002(6)	0.002(6)	-0.011(5)
O22	0.062(6)	0.050(6)	0.032(5)	-0.001(4)	-0.002(4)	-0.018(5)





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LETTERS

## Exploration of Nicholas methodology using chiral heterobimetallic cobalt–molybdenum propargylium complexes

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**Abstract**—Nicholas methodology has been used successfully with chiral heterobimetallic cobalt–molybdenum propargylium complexes in the formation of enyne complexes, new stereocentres and heteroatom ring systems, in high yield and moderate diastereoselectivity. © 2002 Elsevier Science Ltd. All rights reserved.

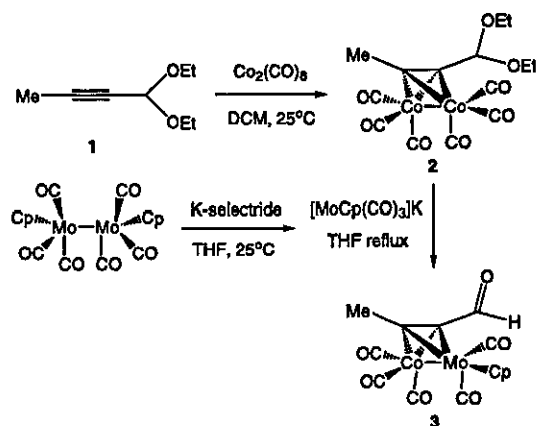
The use of dicobalt hexacarbonyl propargylium complexes in the Nicholas reaction,<sup>1</sup> which involves addition of nucleophiles to complexed propargylic cations, is a widely known and explored method of C–C and C–heteroatom bond formation.<sup>2</sup> This chemistry has been developed with the use of dimolybdenum dicyclopentadienyl tetracarbonyl and diastereomeric dicobalt pentacarbonyl arylphosphite complexes,<sup>3,4</sup> the latter establishing a route to enantiomerically enriched diastereomeric product complexes.<sup>5</sup> Application to the synthesis of ether ring systems has been recognised as a key step in natural product synthesis.<sup>6–10</sup>

Although a great deal of research has been carried out with homobimetallic systems, limited chemistry has been carried out with heterobimetallic propargylium complexes. Examples of interest are the inherently chiral complexes of cobaltmolybdenum cyclopentadienyl pentacarbonyl propargylium complex alkyne[Co–MoCp(CO)<sub>5</sub>], where synthesis and characterisation are known in the literature, but only limited reactivity studies have been reported.<sup>11–17</sup>

With these precedents in mind, we report herein our exploration of the chiral directing capability of the heterobimetallic Co–Mo–alkyne core in nucleophilic attack via the Nicholas approach using propargylic salt complexes both preformed, and formed in situ after protonation of the corresponding enyne. We have also used this methodology in intramolecular nucleophilic additions to form heterocycles. Yields are high, and moderate stereoselectivity is observed.

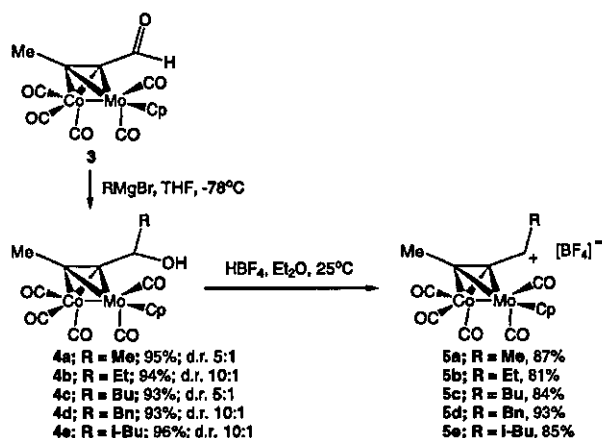
The Co–Mo alkyne aldehyde complex **3** was first prepared by complexation of but-2-ynal diethyl acetal **1** (Co<sub>2</sub>(CO)<sub>8</sub>, DCM, 25°C) to afford **2** (Scheme 1). Isolobal displacement of Co(CO)<sub>3</sub> with MoCp(CO)<sub>2</sub> using the molybdenum anion [Mo(CO)<sub>3</sub>]<sup>−</sup>K (THF reflux, 2 h) and hydrolysis of the diethyl acetal on chromatographic purification led to **3** (86% from uncomplexed acetal **1**).

Grignard reagent addition to the heterobimetallic aldehyde complex **3** at −78°C in THF, as we have previously reported, led to the propargylic alcohols **4a–e** in 93–96% yield and 5:1 to 10:1 d.r.<sup>18</sup> Slow addition of HBF<sub>4</sub> to these alcohols (Et<sub>2</sub>O, 25°C) gave the orange, air stable propargylic salt complexes **5a–e**, respectively, in 81–93% yield (Scheme 2).<sup>19</sup>



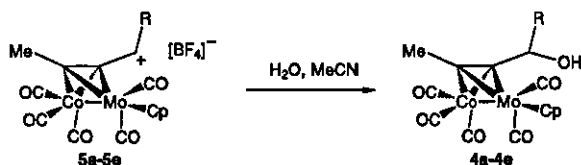
Scheme 1.

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Scheme 2.

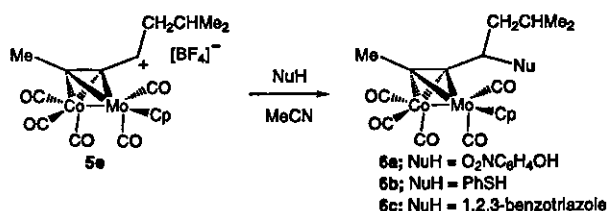
Nucleophilic addition to the propargylic salts **5** was examined using water over a range of solvents and temperatures. Optimum conditions were found to be in MeCN at  $-40^{\circ}\text{C}$  (Scheme 3). Interestingly, the relative d.r. of the returned alcohol complexes **4a–e** (Table 1, entries 1–5) was reversed compared to those isolated from the Grignard addition reaction (Scheme 2), thus enabling access to both alcohol diastereoisomers, which are separable by column chromatography. In the case of benzyl substituted cation **5d**, the corresponding alkene **7d** (see below) was isolated.



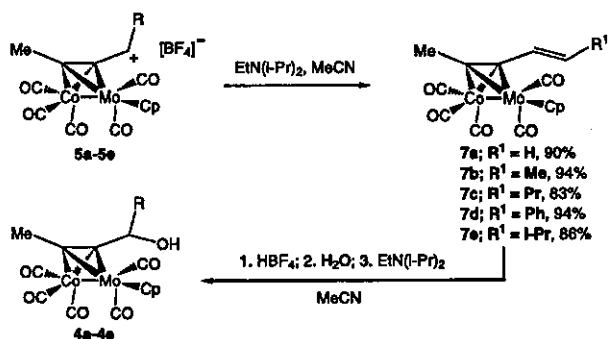
Scheme 3.

As the highest diastereoselectivity was found with the isobutyl substrate **5e**, additions with different heteroatom nucleophiles were carried out using this salt (Scheme 4). Excellent yields of **6a–c** were achieved; diastereoselectivity was moderate but improved at  $-40^{\circ}\text{C}$  relative to room temperature (Table 1, entries 6–11).<sup>20</sup> The diastereoisomers were not separable by standard column chromatography, and all products formed were oils, hence diastereoselectivities were confirmed using 250 MHz  $^1\text{H}$  NMR spectroscopy.

When the propargylic salt complexes **5a–e** were treated with the mild base *N*-ethyldiisopropylamine (Hünig's base) (MeCN,  $25^{\circ}\text{C}$ ), the corresponding *trans* enynes **7a–e** were obtained in 83–94% yield (Scheme 5).<sup>22,23</sup>



Scheme 4.



Scheme 5.

Table 1. Nucleophilic capture of propargylic salt complexes **5** and alkene complexes **7**

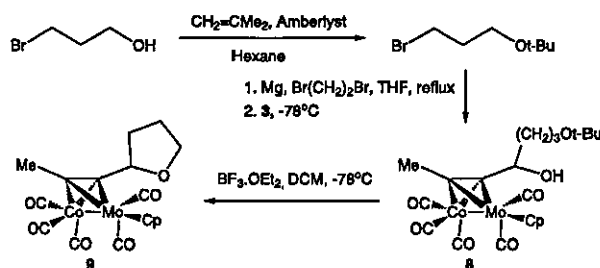
Entry	Complex	Product	Nucleophile	<i>T</i> ( $^{\circ}\text{C}$ )	Yield (%)	D.r.
1	5a	4a	$\text{H}_2\text{O}$	$-40$	68	1:3
2	5b	4b	$\text{H}_2\text{O}$	$-40$	62	1:5
3	5c	4c	$\text{H}_2\text{O}$	$-40$	64	1:4.5
4	5d	(4d)	$\text{H}_2\text{O}$	$-40$	78	(Alkene <b>7d</b> isolated)
5	5e	4e	$\text{H}_2\text{O}$	$-40$	70	1:6
6	5e	6a	4-Nitrophenol	25	58	1:1.5
7	5e	6a	4-Nitrophenol	$-40$	89	1:2
8	5e	6b	PhSH	25	90	1:2
9	5e	6b	PhSH	$-40$	93	1:4
10	5e	6c	1,2,3-Benzotriazole	25	91	1:1
11	5e	6c	1,2,3-Benzotriazole	$-40$	95	1:3
12	7a	4a	$\text{H}_2\text{O}$	25	59	1:2
13	7b	4b	$\text{H}_2\text{O}$	25	61	1:3
14	7c	4c	$\text{H}_2\text{O}$	25	66	1:5
15	7d	4d	$\text{H}_2\text{O}$	25	30	1:1
16	7e	4e	$\text{H}_2\text{O}$	25	65	1:5

As only **7b** showed any sign of a *cis* enyne by  $^1\text{H}$  NMR spectroscopy, this indicated that more highly substituted R-groups favour *trans* enyne formation. This useful preparation of the enyne complexes bypasses the enynes themselves, and may be valuable in synthesis.<sup>21</sup>

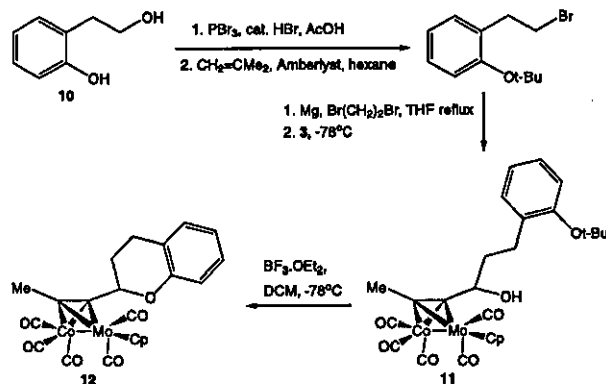
We wished to determine whether addition of a nucleophile to the propargylic carbon atom of the alkenes **7** would be possible and would give results matching direct addition to the salt complexes **5**. Complexes **7a–e** were thus treated successively with  $\text{HBF}_4$  (MeCN,  $25^\circ\text{C}$ ), water and Hünig's base (Scheme 5). Alcohol complexes **4a–e** were indeed recovered (Table 1, entries 12–16); yields were lower than direct addition of water to the salt complexes **5**, with recovery of 10–40% of alkene. The alcohol complexes **4** had equivalent or lower d.r. than from direct addition to the salt complexes **5**, in the same direction (Table 1). It is thus likely that the reactions proceed via the same transition state. Benzyl substituted alcohol **4d** was retrieved in only 30% yield from a mixture; non-regiospecific protonation and stability (conjugation) of alkene **7d** may be factors here.

We wished to demonstrate the scope of this methodology for assembly of diastereomerically enriched heterocyclic rings of varying size via intramolecular nucleophile capture. Thus, we first prepared simple substrate **8** from 3-bromo-1-propanol by protection as the *tert*-butyl ether (2-methylpropene, Amberlyst, hexane),<sup>24</sup> generation of the Grignard reagent (Mg, cat. 1,2-bromoethane, THF reflux) and addition to the aldehyde complex **3** in good yield and d.r. (89%, 7:1) (Scheme 6). Initial trials with THP and *tert*-butyldimethylsilyl protecting groups were unsuccessful. A series of Lewis acids was examined for deprotection–ring closure. TFA,  $\text{TiCl}_4$  and  $\text{HBF}_4$  all formed the corresponding alkene by water loss, but on reaction with  $\text{BF}_3\cdot\text{OEt}_2$  (DCM,  $-78^\circ\text{C}$ ) the tetrahydrofuran **9** was isolated (79%) with reduced d.r. (2:1), as observed by  $^1\text{H}$  NMR spectroscopy.<sup>25</sup>

As a pilot study of six-ring formation, we decided to make the unsubstituted dihydrobenzopyran **12** (Scheme 7). Bromination of the primary alcohol of **10** ( $\text{PBr}_3$ , cat.  $\text{HBr}$ ,  $\text{AcOH}$ ; 49%) was followed by protection of the phenol as its *tert*-butyl ether as above (54%), generation of the Grignard reagent and subsequent addition to **3** to furnish complex **11** in 75% yield and d.r. 7:1. The cyclisation product **12** was formed on treatment



Scheme 6.



Scheme 7.

with  $\text{BF}_3\cdot\text{OEt}_2$  (DCM,  $-78^\circ\text{C}$ ) in 20% yield (unoptimised) and d.r. 1:2.

To conclude, preliminary studies using Nicholas methodology with inherently chiral heterobimetallic Co–Mo propargylium complexes have demonstrated the generation of new propargylic centres by nucleophilic addition in high yields with moderate to good stereoselectivity, and of enyne complexes. Intramolecular nucleophilic capture to form heterocycles shows promise and development is continuing in this area, including extension to nitrogen heterocycles.

### Acknowledgements

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19. **Typical procedure: salt complex 5e.** To cobalt molybdenum alcohol complex **4e** (1.50 g, 3.10 mmol) in dry diethyl ether (40 mL) stirred under nitrogen was added dropwise tetrafluoroboric acid (54 wt.%; 0.60 mL, 4.30 mmol). The reaction mixture was stirred for a further 10 min before the precipitated orange solid was filtered, washed with dry diethyl ether (60 mL) and dried under reduced pressure to yield the salt **5e** as an orange solid (1.59 g, 93%). IR (KBr)/cm<sup>-1</sup> 2045, 1974, 1932. mp = 87–88°C (dec.). Found: C, 38.43; H, 3.21%. C<sub>18</sub>H<sub>18</sub>O<sub>5</sub>–BCoF<sub>4</sub>Mo requires C, 38.88; H, 3.26%.
20. **Typical procedure: complex 6b.** To Co–Mo salt complex **5e** (435 mg, 0.78 mmol) in dry acetonitrile (20 mL) stirred under nitrogen at –40°C was added thiophenol (0.12 mL, 1.17 mmol). The reaction mixture was stirred for 30 min at –40°C, before addition of Hünigs base (0.20 mL, 1.56 mmol). The reaction mixture was allowed to warm to 25°C before filtration through a pad of Celite and silica. The solvent was removed in vacuo to leave a red oil, purified by flash silica chromatography eluting with light petroleum:diethyl ether (10:1 v/v) to yield the complex **6b** as a red oil (420 mg, 93%, 1:4 mixture of diastereoisomers). IR (film)/cm<sup>-1</sup> 2044, 1970, 1933. Major diastereoisomer: <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>) 7.41–7.20 (5H, m), 5.20 (5H, s), 4.50–4.40 (1H, m), 2.69 (3H, s), 2.09–1.92 (1H, m), 1.72–1.56 (2H, m), 0.92 (6H, dd, *J* = 2, 7 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) 226.9, 225.1, 204.8, 138.1, 130.4, 129.4, 126.7, 100.8, 92.6, 90.9, 55.2, 48.5, 26.5, 23.6, 22.1, 21.5. Minor diastereoisomer: <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>) 7.41–7.20 (5H, m), 5.40 (5H, s), 4.50–4.40 (1H, m), 2.56 (3H, s), 2.09–1.92 (1H, m), 1.72–1.56 (2H, m), 0.89 (6H, m). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) 227.1, 225.0, 204.8, 137.8, 130.8, 129.5, 126.8, 101.7, 93.7, 90.9, 54.6, 48.9, 26.2, 23.8, 21.9, 21.4. Found: M<sup>+</sup>–3CO, 495.98165. C<sub>21</sub>H<sub>23</sub>O<sub>2</sub>CoMoS requires 495.98070.
21. See, for example: Caddick, S.; Delisser, V. M. *Tetrahedron Lett.* **1997**, *38*, 2355–2358; Melikyan, G. G.; Khan, M. A.; Nicholas, K. M. *Organometallics* **1995**, *14*, 2170–2172.
22. Cf in Co–Co system: Nicholas, R. M.; Pettit, R. J. *Organomet. Chem.* **1972**, *44*, C21–C24.
23. **Enyne complex 7e.** To Co–Mo salt complex **5e** (100 mg, 0.18 mmol) in dry acetonitrile (10 mL) stirred under nitrogen at 25°C was added Hünigs base (0.05 mL, 0.36 mmol). The reaction mixture was stirred for 30 min before filtration through a pad of Celite and silica. The solvent was removed in vacuo to leave a red oil, purified by flash silica chromatography eluting with light petroleum:diethyl ether (15:1 v/v) to yield the enyne complex **7e** as a red oil (72 mg, 86%). IR (film)/cm<sup>-1</sup> 2959, 2045, 1968, 1885. <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>) 6.34 (1H, d, *J* = 15 Hz), 5.67 (1H, dd, *J* = 7, 22 Hz), 5.33 (5H, s), 2.65 (3H, s), 2.47–2.34 (1H, m), 1.03 (6H, d, *J* = 6 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) 226.3, 225.5, 203.9, 141.8, 126.2, 91.1, 90.0, 31.5, 22.7, 22.6, 21.4. Found: M<sup>+</sup>, 469.9462. C<sub>18</sub>H<sub>17</sub>O<sub>5</sub>CoMo requires 469.9462.
24. Alexakis, A.; Gardette, M.; Colin, S. *Tetrahedron Lett.* **1988**, *29*, 2951–2954.
25. **Tetrahydrofuran complex 9.** To Co–Mo complex **8** (200 mg, 0.37 mmol) in dry DCM (15 mL) stirred under nitrogen at –78°C was added BF<sub>3</sub>·OEt<sub>2</sub> (0.14 mL, 1.11 mmol). The reaction mixture was stirred for 30 min and H<sub>2</sub>O (0.2 mL) was added before filtration through a pad of Celite and silica, washing with DCM and EtOH. The solvents were removed in vacuo to leave a red oil, purified by flash silica chromatography eluting with light petroleum:diethyl ether (10:1 v/v) to yield the tetrahydrofuran **9** as a red oil (136 mg, 79%, 2:1 mixture of diastereoisomers). IR (film)/cm<sup>-1</sup> 2044, 1969, 1926. Major diastereoisomer: <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>) 5.44 (5H, s), 4.82 (1H, t, *J* = 7 Hz), 3.94–3.75 (2H, m), 2.68 (3H, s), 2.24–2.11 (1H, m), 2.02–1.87 (2H, m), 1.71–1.57 (1H, m). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) 226.6, 224.9, 204.4, 98.4, 91.2, 90.2, 83.0, 67.9, 34.0, 26.7, 20.1. Minor diastereoisomer: <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>) 5.41 (5H, s), 4.98 (1H, t, 7 Hz), 3.94–3.75 (2H, m), 2.70 (3H, s), 2.24–2.11 (1H, m), 2.02–1.87 (2H, m), 1.71–1.57 (1H, m). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) 226.0, 225.2, 204.4, 98.5, 91.8, 90.2, 83.1, 68.0, 33.2, 26.6, 20.6. Found: M<sup>+</sup>–CO, 443.93075. C<sub>16</sub>H<sub>15</sub>O<sub>5</sub>CoMo requires 443.93055.



